A Textbook of Physical Chemistry

K K Sharma
L K Sharma

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A TEXTBOOK OF PHYSICAL CHEMISTRY

By the same author

Problems in Physical Chemistry
Problems in Organic Chemistry (Co-authors)
An Introduction to Practical Chemistry (Co-authors)

A TEXTBOOK OF
PHYSICAL CHEMISTRY

[FOR B.SC. (PASS AND HONS.) STUDENTS OF INDIAN UNIVERSITIES]

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PREFACE

The eighth edition of this book is the result of major additions and rewriting of the bulk of the material given in this book.

Specifically the changes have been directed towards the aim to give more rigorous and extensive treatment to atomic structure. The chapter on Chemical Bonding has been completely changed, and major changes have been made in the chapters on Chemical Thermodynamics and Physical Properties and Chemical Constitution. A new chapter on Macromolecules has been added in this edition. Extensive rearrangements, amplification and rewriting of the previous material have been done in this edition.

A large number of solved and unsolved problems have been added. The book covers the revised syllabi of physical chemistry for B.Sc. and B.Pharm. courses of Indian Universities.

We are grateful to our conferrers who contributed so generously with their valuable suggestions to improve the book.

K.K. SHARMA
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PREFACE TO THE FIRST EDITION

The students of Chemistry at the university level are exposed to heavy doses of descriptive and theoretical material, which make it difficult for them to grasp the subject. We, therefore, thought it desirable to restructure the subject-matter in the field of Physical Chemistry in a way that would not only sustain the interest of the students but would also lay particular stress on the stimulating theoretical basis of the modern chemistry. The present work is the result of our efforts in this direction. It is primarily intended to serve as a textbook for B.Sc. General and Honours students. At the same time, the students pursuing M.Sc., Chemical Engineering and other professional courses will also find the book extremely useful.

At the present stage of chemical sophistication, it is not easy to decide the level and the standard of treatment of the subject-matter. However, our main concern in this work is modern chemical theory and not its practical applications.

It has been our attempt to give each of the broad areas of the subject—thermodynamics, structure of the atom and chemical kinetics—a unified treatment. The abstract thermodynamic concepts have been explained with the help of common examples and illustrated further with the help of solved examples.

The treatment of atomic structures and valency is based on electronic energy levels, atomic orbitals and the valence bond approach. The chapter on chemical kinetics has been designed; not merely to state the reaction rate law, but to provide a detailed treatment of the variation of the rate of a reaction with concentration and temperature and the theories of reaction rates.

The chapters on nuclear chemistry, solids, photochemistry, colloids and electrochemistry contain the recent advances made in these fields.

The text is functionally illustrated with over two hundred diagrams and photographs. A large number of thought-provoking problems have been given at the end of each chapter.

We are grateful to the earlier authors in the subject who have shaped our thoughts on various topics. Our gratitude is also extended to our colleagues, friends as also to our students, for their invaluable general helpfulness and many constructive suggestions. Comments and criticism from the readers will be most welcome.

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Chapter 1

SOME FUNDAMENTAL CHEMICAL CONCEPTS

1.1. INTRODUCTION

The collection of facts and theories about natural phenomena and objects, is the body of knowledge called science.

All the scientific knowledge may be grouped into two large divisions: the *biological sciences* which are concerned with living things, their structure, life processes and environment; and the *physical sciences* which deal with the natural relationship about us.

Chemical substances are the material constituents of all the matter in the universe. They are as much the components of living cells as they are the materials that constitute the rocks, liquids and gases of the earth and the rest of the Universe.

Chemistry is the science that describes the structure and composition of the material in the Universe, the changes in structure and composition, this material undergoes and the energy relations involved in these changes.

Chemistry developed from two sources (*i*) philosophical, and (*ii*) utilitarian. Greek philosophers sought to account for the material diversity of the world in orderly and intellectually satisfying terms.

Practical men and women of the several ancient civilisations expanded arts and crafts into useful technologies for smelting and alloying metals, making glass, compounding medicines etc.

Physical chemistry is that branch of chemistry which concerns itself with the study of the physical properties, structure of matter and the laws governing the chemical interactions. The important purpose of physical chemistry is, first, to collect the experimental data, needed to define the properties of gases, liquids, solids, solutions and colloidal dispersions and to provide them a theoretical foundation in the form of laws.

1.2. DEFINITIONS OF SOME CHEMICAL TERMS

In all the discussions in this book any material object whether simple or complex will be referred to as *matter*. A form of matter which cannot be further broken down to simpler forms by ordinary means is known as *element*. The smallest part of an element which can exist in a chemical change is called *atom*. The atoms of a particular element have a definite mass which is different for different elements. Ordinary hydrogen has one unit of mass. It is referred to as atomic mass unit (amu).

All atoms are composed of a nucleus, containing protons and neutrons and a number of electrons outside the nucleus. The number of protons within the nucleus is called the *atomic number* of the element. Substances with the same atomic number but with different mass numbers are known as *isotopes*. Elements, as they occur in nature, may consist of a mixture of isotopes. On the other hand, there are some substances which have same atomic weight but different atomic number. These substances are known as *isobars*.

The atomic weights are expressed in atomic mass unit, the actual numbers used can be thought of as representing the relative weights of the atoms. The listed values of the weights in any weight unit—grams, pounds, tonnes etc., can be associated with these relative weights. If the units chosen for a certain use is grams, the resulting quantities are known as gram-atomic weights. The exact gram-atomic weight of an element is the number of grams of that element numerically equal to its atomic weight in atomic mass unit (amu).

The table of atomic weights is a compilation of masses of the elements relative to the $O^{16} = 16.00000000$. In 1961, the International Union of Pure and Applied Chemistry adopted a new atomic weight system based on the C^{12} isotope of carbon as being 12.00000.

The smallest particle of a substance capable of independent existence as a gas or as a definite entity in solution is called a *molecule*. The weight of a molecule can be obtained by adding the atomic weights of all the atoms in it.

The weight of a substance expressed in grams is known as the *gram molecular weight* or more simply as *mole*. Since molecular formula of oxygen is O_2, 32 grams of oxygen is equivalent to 1 mole. Similarly one mole of hydrogen weighs 2 grams. A mole contains 6.023×10^{23} number of molecules. This number is called *Avogadro's number*. The relationship between moles and molecules is:

n (moles) $\times N$ (Avogadro's Number) $=$ Total number of molecules.

1.3. STATES OF MATTER

Matter exists in three main states—gaseous, liquid and solid. The main difference in the three states lies in the arrangements of atoms, molecules or ions constituting the matter. In solids, the molecules are most closely packed and are orderly arranged. The stronger cohesive forces in a solid are responsible for its higher density, hardness, strength and ability to resist the effects of heating with the exception of ice. Moreover, compactness of the molecules is responsible for the definite shape and volume at a given temperature and pressure for every solid. In gaseous state, the molecules are not orderly arranged. The molecules in a gas are far apart and are moving at a very high speed in all directions. Gases, therefore, possess neither definite volume nor shape and fill completely any container in which they are placed. In liquids, molecules are not as close as in the solid but are much closer than are the molecules in a gas. The liquid is intermediate between the solid and the gas and hence its properties are intermediate between those of the other two states. A liquid has a definite volume but no definite shape. It always adopts the shape of the container. Both gases and liquids are termed as *fluids*.

The above distinctions in the three states of matter is not absolute. The distinction is physical and can be observed with any substance which changes its physical state by changing temperature and pressure without changing its chemical nature. For example, ice, liquid water and water vapors are chemically similar as they are all composed of H_2O molecules. The difference in the three forms of water is due to the difference in the compactness of molecules in the three states. Moreover certain substances, such as glass, gels, rubber and plastic are not properly classified by implying the above definitions, *e.g.*, rubber when stretched exhibits many of the properties of a solid whereas in its normal state, it does not exhibit the property of a solid.

At a certain temperature and pressure, it is not always possible to clearly distinguish the three states of matter, *e.g.*, at critical point, a liquid cannot be distinguished from its vapor. Similarly glass, which exhibits many of the properties of a solid, becomes plastic on heating to a high temperature and exhibits properties entirely different from solid. For this reason, glass and similar substances are known as supercooled liquids with very high viscosity.

The particular state of aggregation of matter is determined by the temperature and pressure under which the substance exists. It is also possible that a substance may exist together in more than one form at a certain temperature and pressure. For example, at the tripple point (temperature=0.010°C and pressure=4.57 mm Hg), all the three states of water are present together.

Properties of matter, useful in identifying it, are called specific properties and may be classified under two general headings: *physical* and *chemical*.

Physical properties are those which can be determined without causing a change in the identity of a material. These include colour, odour, solubility, density, hardness, melting and boiling points and crystalline or amorphous forms.

Chemical properties are those which deal with the behaviour of a material in changes in which its identity is altered.

Matter can be converted to energy and energy to matter. However, matter and energy may be considered to be two different forms of the same physical quantity. This can be formulated into the *Law of Conservation of Matter and Energy*. It can be stated as, "matter and energy are interchangeable; and the total matter and energy in the universe is constant."

Force, Pressure and Energy

The concepts of force, pressure and energy are very important in Physical Chemistry. It would therefore be useful if we familiarise ourselves with their S.I. units.

Force. The basic unit of force, is, the force necessary to move a mass of 1 kg so that it accelerates at the rate of 1 ms^2. The basic unit is newton ($1N=1$ kg ms^{-2}).

Pressure. When a force 1N is acting on an area of $1m^2$, gives us the basic unit of pressure. It is called Pascal ($1Pa=1Nm^{-2}$). One atm is exactly 101325 Nm^{-3} but one atm$\approx 10^5$ Nm^{-2} is often sufficiently accurate.

The other common unit of pressure is Torr (named after Torricelli who invented the barometer). The Torr is just another name for mm Hg. 1 atm=760 Torr. Pressure is also expressed in bar (1 bar= 10^5 Nm^2).

Energy. The unit for measuring energy is the joule (J). The formal definition of 1J is that it is the energy required to push against force of 1N for 1m ($1J=1Nm$). One of the most common unit of energy is the thermochemical calorie (cal). This is defined as 4.184J. Another unit of energy is the electron volt (eV). This is the energy acquired by an electron when it is accelerated through a potential of 1V. Since in chemical reactions one is dealing with molar quantities, it is better to think in terms of 1 mol of electrons. The conversion is 1 eV=96.49 kJ mol^{-1} ($\simeq$100 kJ mol^{-1}).

Chapter 2

GASEOUS STATE

Evangelista Torricelli, in 1643, advanced the concept that we live in a deep sea of air which has weight that presses upon us. He showed that a column of mercury can be employed for its measurement.

In the gaseous state which is the simplest of the three states of aggregation of matter, the arrangement of molecules at any time is random or disorderly. There are two types of gases, namely, (*a*) *ideal gases*, and (*b*) *non-ideal* or *real gases*.

A gas is said to be ideal if it obeys the gas laws such as Boyle's law and Charles's law at all temperatures and pressures. A real gas obeys these laws only at low pressures and high temperatures.

In an ideal gas, the volume occupied by the gas molecules is negligibly small as compared with the total volume at all temeratures and pressures and the molecules exert no attractive or repulsive forces on each other. For non-ideal or real gases, both of these factors are appreciable and the magnitude of each of them will depend on the nature, temperature and pressure of the gas. There is no gas which behaves ideally at all temperatures and pressures and is just a hypothetical concept because the molecules of every gas do occupy some volume and exert some attractive or repulsive forces on each other. However, when the temperature is very high and the pressure is very low, the influence of these factors becomes so small that they are negligible and the gas is considered to approach the ideal behaviour.

2.1. THE LAWS GOVERNING THE IDEAL GAS BEHAVIOUR

Boyle's Law. This law, given by Robert Boyle in the year 1662, states that *temperature remaining constant, the volume* (V) *of a given quantity of a gas varies inversely as the pressure* (P) *on the gas.* That is:

$$V \propto \frac{1}{P} \qquad \text{(At constant temperature)}$$

or

$$V = \frac{K_1}{P}$$

where K_1 is a constant of proportionality, the magnitude of which depends on the temperature, the weight of the gas, its nature and units in which P and V are expressed. Alternatively, this equation can be written as:

$$PV=K_1 \qquad \ldots (2.1)$$

Equation (2.1) is the equation of a hyperbola and the curve plotted between pressure and volume should yield a hyperbola. This is shown in Fig. 2.1 for three temperatures T_1, T_2, T_3, where T_3 is greater than T_2 and T_2 is greater than T_1 for the same amount of a gas.

Each curve has a different value for K_1 because temperature is different and is known as isotherm. (iso=same; therm=temperature).

Equation (2.1) can be written in the more useful form as follows:

Let P_1 and V_1 be the pressure and volume of a given mass of a gas in certain state while in another state they are P_2 and V_2. Temperature in both the states is constant. Since the product of pressure and volume must equal a constant at a definite temperature, it follows that:

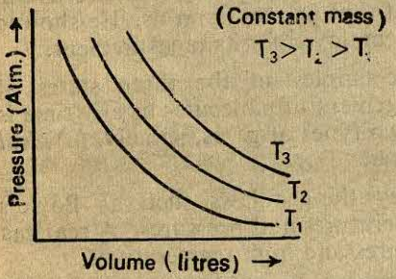

Fig. 2.1. Volumes as a function of pressure at constant temperature.

$$P_1V_1=P_2V_2=K_1 \qquad \ldots (2.2)$$

If any three of these variables are known, the fourth one can be calculated from the equation (2.2).

Charles's or Gay-Lussac's Law—Absolute Temperature. This law deals with the variation of volume with temperature at constant pressure. Charles, in 1787, observed that at constant pressure, the volume of any gas expanded by the same fraction of its initial volume at 0°C for every one degree centigrade rise in temperature. Charles's work was confirmed by Gay-Lussac in 1802. Gay-Lussac found that for each degree rise in temperature, the volume of the gas increased by approximately 1/273 of the volume of the gas at 0°C. The more accurate value of this fraction is:

1/273.15.

If V_0 is the volume of the gas at 0°C and V is the volume at any temperature t°C, then according to the above statement:

$$V_t=V_0+\frac{t}{273.15}V_0$$

$$=V_0\left(1+\frac{t}{273.15}\right)$$

or

$$=V_0\left(\frac{273.15+t}{273.15}\right) \qquad \ldots (2.3)$$

The quantity $(273.15+t)$ is defined as the *absolute* or *Kelvin temperature*. Thus, T (K or Å)$=273.15+t$ (°C). Thus to obtain the temperature T on the absolute scale from the temperature t on the centigrade scale, one adds 273.15 to the centigrade temperature. Similarly, the temperature at 0°C is given by $T_0=273.15$. When $T=-273.15$°C. $T=0$ K which is the lowest temperature attainable. In terms of absolute scale, equation (2.3) becomes:

$$\frac{V_t}{V_0}=\frac{T}{T_0}$$

or in general

$$\frac{V_2}{V_1}=\frac{T_2}{T_1} \qquad \ldots (2.4)$$

According to equation (2.4), *volume for any definite quantity of a gas at constant pressure is directly proportional to the absolute temperature.* Mathematically: $V \propto T$ (at constant pressure)

or

$$V=K_pT \qquad \ldots (2.5)$$

where K_p is a constant of proportionality and depends upon the pressure, mass and nature of the gas and the units of V. This is an alternate expression of Charles's or Gay-Lussac's Law of volume.

According to equation (2.5), a graph of volume versus absolute temperature for any definite quantity of gas at constant pressure should be a straight line. Fig. 2.2 shows a plot of volume versus temperature at two pressures; P_1 and P_2 $(P_2>P_1)$ for the same quantity of a gas. The value of K_p for each of these two plots will be different. The constant pressure curve is called an *isobar*. It is clear from the curve that greater is the pressure, the lower is the slope.

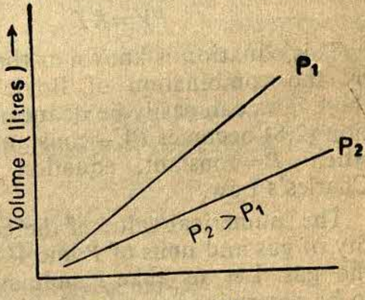

Fig. 2.2. Volume as a function of temperature at constant pressure.

Equation (2.5) also suggests that if $T=0$ $(-273°\text{C})$, $V=0$. But actually this condition can never be achieved because before such a low temperature is achieved, every gas gets liquefied or solidified.

2.2. THE COMBINED GAS LAW AND THE GAS EQUATION

The two gas laws discussed above can be combined into one law as follows:

Let P_1, V_1 ond T_1 be the pressure, volume and temperature respectively of any definite quantity of a gas and let it be desired to have it at P_2, V_2 and T_2. This is achieved in two steps:

(*i*) The pressure P_1 is changed to P_2 at constant temperature T_1

by compressing or expanding the gas. The resulting volume V_x, according to Boyle's Law, is given by:

$$V_x=\frac{P_1V_1}{P_2} \qquad \ldots (2.6)$$

(*ii*) The temperature is changed from T_1 to T_2 keeping the pressure P_2 constant and during this change let the volume change from V_x to V_2. According to Charles' Law, at constant pressure, we have:

$$\frac{V_x}{V_2}=\frac{T_1}{T_2} \quad \text{or} \quad V_r=\frac{V_2T_1}{T_2} \qquad \ldots (2.7)$$

Substituting the value of V_x from equation (2.7) into equation (2.6), we get:

$$\frac{V_2T_1}{T_2}=\frac{P_1V_1}{P_2}$$

or

$$\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}=\text{Constant } (k)$$

In general, $\frac{PV}{T}=K$ *i.e.* the ratio $\frac{PV}{T}$ for any definite quantity of a gas obeying Boyle's Law and Charles's Law is constant.

On rearranging:

$$PV=KT \qquad \ldots (2.8)$$

This equation is known as the combined gas law as it is obtained by the combination of Boyle's Law and Charles's Law and both these laws can easily be deduced from this. When T=constant, equation (2.8) becomes PV=constant which is Boyle's Law. Similarly, when P=constant, equation (2.8) reduces to $V \propto T$ which is Charles's Law.

The numerical value of the constant K is determined by the quantity of gas and units of P and V but is independent of the nature of the gas. Let us take 1 mole as the quantity of gas whose volume is to be determined at some fixed temperature and pressure, say 0°C (273.15 K) and one atmosphere respectively—the so-called standard temperature and pressure (STP). Now, according to Avogadro's Law, one mole of every gas under these standard conditions of temperature and pressure occupies the same volume (22.414 litres).

Let P_0, V_0 and T_0 be the pressure, volume and temperature respectively of the gas at STP, then for 1 mole of gas:

$$\frac{P_0V_0}{T_0}=\frac{PV}{T}=R \text{ (constant)} \qquad \ldots (2.9)$$

where R is a universal constant for all gases and is known as the gas constant.

For n moles, equation (2.9) becomes

$$PV=nRT \qquad \ldots (2.10)$$

This equation is known as the *ideal gas equation*.

2.3. NUMERICAL VALUES OF *R*

This can be easily found from the fact that 1 mole of any ideal gas at STP occupies a volume of 22.414 litres.

Therefore, $$R=\frac{PV}{nT}=\frac{1\times 22.414}{1\times 273.15}$$

$$=\frac{0.0821 \text{ litre atm/degree}}{1 \text{ mole}}$$

If volume is expressed in cubic centimetres,

$$R=\frac{1\times 22.414}{1\times 273.15}=82.1 \text{ cm}^3 \text{ atm/degree/mole}$$

Again, since $$R=\frac{\text{Pressure}\times\text{volume}}{\text{Number of moles}\times\text{temperature}}$$

$$=\frac{\frac{\text{Force}}{\text{Area}}\times\text{Area}\times\text{length}}{\text{moles}\times\text{degree}}$$

$$=\text{Work/Degree/mole.}$$

Therefore, *R* can also be expressed in any set of units representing work or energy.

In CGS units, when it is desired to determine the value of *R* in ergs, pressure should be expressed in dynes/square centimetres and volume in cubic centimetres. The values of *P* and *V* in CGS units are given by:

$$P=1\times 76\times 13.595\times 981 \text{ dynes/cm}^2 \text{ at } 0°\text{C}$$

(13.595 is the density of mercury at 0°C)

$$V=22.414 \text{ cc.}$$

Therefore, $$R=\frac{(76\times 13.595\times 981)(22.414)}{1\times 273.13}$$

$$=8.314\times 10^7 \text{ ergs/degree/mole.}$$

Further, since 1 Joule $=10^7$ ergs and 1 calorie $=4.184$J

$$R=8.314 \textit{ joules/degree/mol}$$

and also $$R=\frac{8.314}{4.184}=1.987 \text{ calories/degree/mol}$$

Values of *R* may be summarised as under:

$$R\left\{\begin{array}{l}\textbf{0.082 litre atm/deg/mol}\\ \mathbf{8.314\times 10^7} \textbf{ ergs/deg/mol}\\ \textbf{8.314 joules/deg/mol}\\ \textbf{1.987 calories/deg/mol}\end{array}\right\}$$

Sl units

The modern value of $V=22.41383$ L/mol

$=22.41383\times 10^{-3}$ m^3/mol. Since $T=273.15$ K,

$P=1$ atm $=1.01325\times 10^5$ *Pa* the value of *R* is

$$R=\frac{PV}{T}=\frac{(1.01325\times10^5\ Pa)(22.41383\times10^{-3}\ \mathrm{m^3/mol})}{298.15}$$

$$=8.31441\ Pa\ \mathrm{m^3\ K^{-1}\ mol^{-1}}=8.31441\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

R has the dimensions of energy kelvin^{-1} mole^{-1}. The SI unit of pressure is the pascal (Pa) defined by

$$1Pa=1N/\mathrm{m^2}=1\ \mathrm{J/m^3}=1\ \mathrm{kg\ m^{-1}\ s^{-2}}$$

The common practical units of pressure are the atmosphere (atm), the torr (Torr) and the millimetre of mercury (mm/Hg). The standard atmosphere is defined by

$$1\ \mathrm{atm}=1.01325\times10^5\ Pa$$

The torr is defined

$$760\ \mathrm{Torr}=1\ \mathrm{atm}$$

The conventional millimetre of mercury (mm Hg) is the pressure exerted by a column of mercury 1 mm high of a fluid having a density of exactly 13.5951 g/cm^3 in a location where the acceleration of gravity is exactly 9.80665 m/s^2. The millimetre of mercury is greater than the torr by about 14 parts in 10^8. For our purposes 1 mm Hg=1 Torr.

The SI unit of volume is the cubic metre. The practical units of volume are the cubic centimetres and the litre L. The relations are

$$1L=1\ \mathrm{dm^3}=1000\ \mathrm{cm^3}=10^{-3}\ \mathrm{m^3}$$

Problem 2.1. One mole of an ideal gas occupies 12 L at 25°C. What is the pressure of the gas?

Solution

$$P=\frac{nRT}{V},\ T=273.15+25=298.15\ \mathrm{K}$$

$$V=12\ L\times10^{-3}\ \mathrm{m^3}/L=0.012\ \mathrm{m^3}$$

$$P=\frac{1\ \mathrm{mol}\ (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(298\ \mathrm{K})}{0.012\ \mathrm{m^3}}$$

$$=2.06\times10^5\ \mathrm{J/m^3}$$

$$P=2.06\times10^5\ \mathrm{Pa}\qquad=206\ \mathrm{kPa}$$

Problem. 2.2. A 2-litre Dumas bulb contains n moles of nitrogen at 0.5 atm pressure at T K. On addition of 0.01 moles of oxygen, it is necessary to cool the bulb to a temperature of 10°C in order to maintain the same pressure. Calculate n and T.

Solution. For an ideal gas, $PV=nRT$

Therefore, $$n=\frac{PV}{RT}$$

After the addition of oxygen, we have $(n+0.01)=\dfrac{PV}{RT}$

where

$P=0.5$ atm.

$V=2$ litres

$R=0.082$ litre atm deg^{-1} mole^{-1}

$T=283+10=283\mathrm{K}$

$$(n+0.01)=\frac{0.5\times2}{0.082\times283}=0.0332$$

Hence $n=0.0332$

Therefore, $T=\dfrac{PV}{nR}$

$$=\frac{0.5\times2}{0.0332\times0.082}$$

$$=367\ \text{K}.$$

Problem. 2.3. Two flasks of equal volume are connected by a narrow tube (of negligible volume). Initially both flasks are at 27°C and contain 0.70 moles of hydrogen gas, the pressure being 0.50 atm. One of the flasks is then immersed in a hot oil bath at 127°C while the other is kept at 27°C. Calculate the final pressure and the moles of hydrogen in each flask.

Solution. The gas equation $PV=nRT$ can be written as:

$$n=\frac{PV}{RT}$$

In the initial conditions, $n=0.70$ mole

$P=0.5$ atm. and $T=273+27=300$ K.

$$0.7=\frac{0.5\times2V}{R\times300}\ (V \text{ is the volume of one bulb})$$

or $V/R=0.7\times300$

When one flask is heated, the same 0.7 mole will be equal to n_1+n_2,

Thus, $$0.7=\frac{PV}{R}\left(\frac{1}{T_1}+\frac{1}{T_2}\right)$$

$T_1=300$ K and $T_2=400$ K.

On inserting the value of V/R,

$$0.7=P\times0.7\times300\ \left(\frac{1}{300}+\frac{1}{400}\right)$$

or $P=0.57$ atm. **Ans.**

Also $n_1=\dfrac{0.57V}{300R}=\dfrac{0.57\times0.7\times300}{300}=0.40$ mole **Ans.**

Hence $n_2=0.70-0.40=0.30$ mole. **Ans.**

2.4. DALTON'S LAW OF PARTIAL PRESSURE

This law states that *at constant temperature, the total pressure exerted by a mixture of gases in a definite volume is equal to the sum of the partial pressures which each gas would exert if it occupied the same total volume alone.*

Thus in a mixture of gases, each gas would exert its pressure independently of the other gases in the mixture and this individual pressure will be same if the gas is taken separately provided the specified volume and temperature remain constant.

For this law to hold, it is essential that the gases involved in the mixture should not interact chemically or physically and behave ideally.

Consider three gases, say A, B and C, taken separately in a V litre flask at some temperature T and let P_A, P_B and P_C be the respective pressure of each gas. Let all the three gases be forced into another V litre flask at the same temperature. Then, according to Dalton's Law of partial pressure, total pressure (P) in the fourth flask would be:

$$P=P_A+P_B+P_C \qquad \ldots (2.11)$$

P_A, P_B and P_C are the partial pressure of each gas. Applying ideal gas equation:

$$P_A=n_A\frac{RT}{V} \qquad \ldots (2.12)$$

$$P_B=n_B\frac{RT}{V} \qquad \ldots (2.13)$$

and
$$P_C=n_C\frac{RT}{V} \qquad \ldots (2.14)$$

Since the total pressure,

$$P=P_A+P_B+P_C$$

Therefore,
$$P=n_A\frac{RT}{V}+n_B\frac{RT}{V}+n_C\frac{RT}{V}$$

$$=(n_A+n_B+n_C)\frac{RT}{V}$$

$$=n_t\frac{RT}{V} \qquad \ldots (2.15)$$

where $n_t=n_A+n_B+n_C$ is the total number of moles of gas in the mixture.

Dividing equations (2.12), (2.13) and (2.14) by equation (2.15), we get:

$$P_A=\left(\frac{n_A}{n_t}\right)P \qquad \ldots (2.16)$$

$$P_B=\left(\frac{n_B}{n_t}\right)P \qquad \ldots (2.17)$$

and
$$P_C=\left(\frac{n_C}{n_t}\right)P \qquad \ldots (2.18)$$

The terms in the brackets of above equations stand for the number of moles of each gas divided by the total number of moles of all gases present together and are known as the *mole fraction* designated by the symbol X_A, X_B and X_C respectively.

Thus,
$$P_A=X_AP$$
$$P_B=X_BP$$
and
$$P_C=X_CP$$

In terms of mole fraction, the partial pressure of each gas in a mixture of gases is equal to the mole fraction of that gas multiplied by the total pressure.

The sum of all the mole fractions is unity *i.e.*

$$X_A+X_B+X_C=1$$

In Dalton's Law of partial pressure, the gases are mixed at constant volume and temperature. If they are mixed at constant pressure and temperature, the total volume of the resulting mixture is given by the sum of the individual volume *i.e.* $V=V_A+V_B+V_C$ where V is the total volume of the mixture and V_A, V_B and V_C are the partial volumes.

This is known as *Amagat's Law of partial volume*. As in Dalton's Law of partial pressure, it can also be shown that

$$V_A=X_AV,\ V_B=X_BV \text{ and } V_C=X_CV$$

Problem. 2.4. The total pressure exerted by a mixture of two gases A and B is 76.2 cm. The number of moles of the two gases are 0.0075 and 0.0040 respectively. Calculate the partial p essures of the two gases.

Solution. Total number of moles$=0.0075+0.0040=0.0115$

Partial pressure of A,

$$P_A=\left(\frac{n_A}{n_A+n_B}\right)P$$

$$=\frac{0.0075}{0.0115}\times 76.2=49.7 \text{ cm. of Hg.}$$

and partial pressure of B,

$$P_B=P-P_A$$

$$=76.2-49.7=26.5 \text{ cm. Hg.}$$

P_B can also be found from the relationship,

$$P_B=\left(\frac{n_B}{n_A+n_B}\right)P$$

Problem 2.5. If 12.0 gms of N_2 0.40 grams of H_2 and 9.0 grams of O_2 are put into a 1.00 litre container at 27 °C, what is the total pressure in the container?

Solution. The number of moles of each gas is

$$\frac{12.00 \text{ gm } N_2}{28.0 \text{ gm/mole}}=0.43 \text{ mole } N_2$$

$$\frac{0.40 \text{ gm } H_2}{2.0 \text{ gm/ mole}}=0.20 \text{ mole } H_2$$

and $$\frac{9\ 00 \text{ gm } O_2}{32 \text{ gm/mole}}=0.28 \text{ mole } O_2$$

The total number of moles, $n_t=0.43+0.20+0.28=0.91$ mole.

Total pressure, P, is then determined by

$$P=\frac{n_tRT}{V}$$

here, $n_t=0.91$ mole, $T=300$ K

$R=0.082$ litre atm/deg/mole and $V=1.00$ litre

$$P=\frac{0.91\times 0.082\times 300}{1.00}=22.4 \text{ atm.} \quad \textbf{Ans.}$$

The same result can also be obtained by calculating the pressure of the gases indirectly and adding them to give the final pressure.

2.5. GRAHAM'S LAW OF DIFFUSION

Whenever a gas is taken in a container having a small hole, it has a natural tendency to escape that container. However, the rate at which the gas escapes is not the same but would be different for different gases. This tendency is known as the diffusion. Graham's law deals with the diffusion of various gases and states that, *at constant pressure and temperature, the rate of diffusion of any gas is inversely proportional to the square root of the density or the molecular weight of the gas.*

If d_2 and d_1 are the densities of two gases at the same temperature and pressure and r_2 and r_1 are their respective rates of diffusion, then according to Graham's law of diffusion:

$$\frac{r_1}{r_2}=\sqrt{\frac{d_2}{d_1}} \qquad \ldots (2.19)$$

Since the pressure and temperature are the same, the molar volume of each gas would also be same, say, V_m.

Equation (2.19), therefore, can also be written as:

$$\frac{r_1}{r_2}=\sqrt{\frac{d_2V_m}{d_1V_m}}=\sqrt{\frac{M_2}{M_1}} \qquad \ldots (2.20)$$

where M_2 and M_1 are the molecular weights of two gases.

Problem 2.6. What is the relative rate of diffusion for hydrogen molecules compared to those of oxygen at the same temperature?

Solution. According to Graham's law of diffusion:

$$\frac{r_{H_2}}{r_{O_2}}\sqrt{\frac{M_{O_2}}{M_{H_2}}}$$

Here $M_{O_2}=32$ and $M_{H_2}=2$

$$\frac{r_{H_2}}{r_2}=\sqrt{\frac{32}{2}}=\sqrt{16}=4$$

The hydrogen molecules diffuse four times faster than oxygen molecules.

2.6. THE KINETIC THEORY OF IDEAL GASES

The laws governing gaseous behaviour discussed so far were arrived at by experiment and there was no theoretical justification. The kinetic theory of gases, first proposed by Bernoulli (1738) and subsequently developed by Clausius, Clark Maxwell, Boltzmann, van der Waals and others, provides a theoretical explanation for the properties of ideal gases. This theory is based on certain assumptions which cannot be treated as strictly correct.

The essential postulates of kinetic theory of ideal gases are:

(*i*) Every gas consists of a very large number of tiny solid particles called molecules. Molecules of the same gas are identical in all respects *i.e.*, they have the same mass, shape and size but differ from molecules of another gas.

(*ii*) The molecules of a gas within a container are in a state of constant rapid motion in all possible directions. They travel in straight lines until on collision with another molecule or with the walls of the container the direction of motion is changed.

(The average distance that a molecule moves through before colliding with another molecule is known as the mean free path of the molecule and is constant under constant condition of temperature and pressure.)

(*iii*) The pressure of a gas on any surface is the result of continuous bombardment on the surface by its molecules.

It can easily be explained why the pressure is increased by decreasing the volume at constant temperature or raising the temperature at constant volume. In the first case, more molecules are crowded into a given space and in the second case, the velocity of the molecules and, subsequently, their Kinetic energy is increased.

(*iv*) The molecules of a gas exert no appreciable attraction on each other and behave as perfectly elastic body. Hence the collisions of the molecules wlth each other and the walls of the container are perfectly elastic and there is no loss of kinetic energy resulting from their collisions or mutual friction.

(*v*) The absolute temperature of a gas is a measure of the average kinetic energy of all the molecules present in it and is directly proportional to it.

(*vi*) There is no effect of gravity on the motion of the molecules of a gas.

(*vii*) Since the molecules are very small as compared to the distances between them, they may be considered to a first approximation to be point masses with vanishingly small volumes. Hence their actual volume is negligible in comparison with the total volume of the gas.

The postulates (*iv*) and (*vii*) are the weakest assumptions of the theory and embody the model of an ideal gas.

Pressure of an ideal gas. With the aid of these simple assumptions, it is possible to deduce an equation for the pressure of an ideal gas and is derived as follows:

Consider a cubical vessel of each side l with perfectly elastic walls containing a very large number of molecules, say n'. Let m be the mass of each molecule and their velocity is U. (The velocity taken here is known as the root mean square velocity.)

The velocity U can be resolved into three component velocities—U_x, U_y and U_z parallel to the three mutually perpendicular axes—x, y and z and is governed by the relationship:

$$U^2=U_x^2+U_y^2+U_z^2$$

Consider one molecule in the cube, moving in x-direction perpendicular to face A. The molecule strikes the face A with a velocity U_x and momentum mU_x. After striking, it rebounds with the same velocity—U_x and momentum—mU_x in the backward direction.

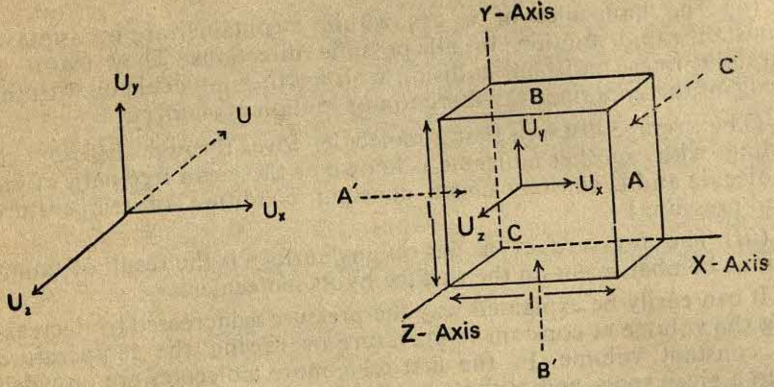

Fig. 2.3. Resolution of velocity along three co-ordinate axes.

Therefore, the change in momentum per molecule per single collision in the x-direction at the face A is

$$=mU_x-(-mU_x)=2mU_x.$$

The molecule now moves to the opposite wall, A'. It strikes A', rebounds and travels back again to A after covering a distance, $2l$. The time taken by the molecule to go to the other side and then to come back is $\frac{2l}{U_x}$.

Hence the number of impacts with the wall A which the molecule will experience per second

$$=\frac{U_x}{2l}.$$

Therefore, change in momentum/second for one molecule at the face A,

$$=(2mU_x).\frac{U_x}{2l}=\frac{mU_x^2}{l}$$

The same change in momentum will be experienced by the same molecule on the opposite face, A'.

Hence, total change in momentum/second/molecule in x-direction

$$=\frac{2mU_x^2}{l} \qquad \ldots (2.21)$$

Similarly change in momentum/second/molecule in the y-direction and z-direction is given by:

$$\frac{2mU_y^2}{l} \text{ and } \frac{2mU_z^2}{l} \text{ respectively.}$$

Hence the total change in momentum/molecule/second for all the three components is:

$$=\frac{2mU_x^2}{l}+\frac{2mU_y^2}{l}+\frac{2mU_z^2}{l}$$

$$=\frac{2m}{l}(U_x^2+U_y^2+U_x^2)$$

or
$$=\frac{2mU^2}{l} \qquad \ldots (2.22)$$

Since there are n' molecules in the cube, total change in momentum/second for n' molecules

$$=\frac{2mn'U^2}{l} \qquad \ldots (2.23)$$

Now, from Newton's second law of motion, rate of change of momentum is the force, f, and force per unit area is defined as the pressure, P.

Therefore,
$$P=\frac{f}{A}=\frac{2mn'U^2}{lA} \qquad \ldots (2.24)$$

Since, the total area of the walls of the cube is $6l^2$

Therefore,
$$P=\frac{2mn'U^2}{l\times 6l^2}=\frac{mn'U^2}{3l^3} \qquad \ldots (2.25)$$

The volume of the cube, $V=l^3$.

$$\therefore \quad P=\tfrac{1}{3}\frac{mn'U^2}{V}$$

or
$$PV=\tfrac{1}{3}\,mn'U^2 \qquad \ldots (2.26)$$

This equation derived by considering a cube relates the pressure of the gas to the volume of the vessel and the mass, number and velocities of the molecules. The same equation can also be deduced by considering the vessel of any other shape.

2.7. DEDUCTION FROM KINETIC THEORY

Gas Laws

(*a*) **Boyle's Law.** According to Boyle's Law, PV=constant (T= constant).

This law can be easily deduced by considering postulate (*v*) of the kinetic theory of gases, according to which kinetic energy for n' molecules, $\frac{1}{2}mn'\,U^2$ is directly proportional to the absolute temperature *i.e.*, $\frac{1}{2}mn'U^2T$

or $$\tfrac{1}{2}mn'U^2=kT \qquad \ldots (2.27)$$

where k is some proportionality constant.

Multiplying the numerator and denominator of the left hand side of this equation by 3, we get $\frac{3}{2}\left(\frac{1}{3}\,mn'U^2\right)=kT$

or $$\tfrac{1}{3}\,mn'U^2=\tfrac{2}{3}kT \qquad \ldots (2.28)$$

But from kinetic theory of gases, $PV=\frac{1}{3}\,mn'U^2$.

Therefore, equation (2.28) becomes:

$$PV=\tfrac{2}{3}\,kT \qquad \ldots (2.29)$$

or $$PV=\text{constant, if } T \text{ is constant.}$$

This is Boyle's Law.

(*b*) **Charles's Law**. According to Charles's Law, $V \propto T$ (P=constant). It has been shown above that $PV=\frac{2}{3}\,kT$. This equation can also be written as:

$V=\frac{2}{3}\,(k/P)\,T$ which reduces to $V \propto T$ if P is constant. This is Charles's Law.

(*c*) **Avogadro's Law**. This law which states that equal volume of two gases under similar conditions of temperature and pressure contain equal number of molecules, is deduced as follows:

For any two gases, 1 and 2, equation (2.26) from kinetic theory of gases is written as:

$$P_1V_1=\tfrac{1}{3}m_1n'_1U_1^2, \text{ and } P_2V_2=\tfrac{1}{3}m_2n'_2U_2^2$$

If pressure and volume of the two gases are equal,

$$P_1V_1=P_2V_2$$

and hence $\frac{1}{3}\,m_1n'_1U_1^2=\frac{1}{3}m_2n'_2U_2^2$ $\qquad \ldots$ (2.30)

Again, if the two gases are at the same temperature, the average kinetic energy/molecule will be same i.e.,

$$\tfrac{1}{2}m_1U_1^2=\tfrac{1}{2}m_2U_2^2 \qquad \ldots (2.31)$$

Combination of equations (2.30) and (2.31) yields $n_1=n_2$ which is Avogadro's Law.

(*d*) **Graham's Law of Diffusion**

Since $$PV=\tfrac{1}{3}\,mn'U^2$$

Rewriting this equation as

$$U^2=\frac{3PV}{mn'} \qquad \ldots (2.32)$$

Again, the density of gas, say

$$d=\frac{mn'}{V}$$

Therefore, equation (2.32) becomes:

$$U^2=\frac{3P}{d} \text{ or } U=\sqrt{\frac{3P}{d}} \qquad \ldots (2.33)$$

From equation (2.33) it follows that $U \propto \frac{1}{\sqrt{d}}$ if pressure is constant.

This is Graham's Law of Diffusion.

Similarly, if two gases are considered at constant volume and pressure, then

$$\tfrac{1}{3}m_1n'_1U_1^2=\tfrac{1}{3}m_2n_2'U_2^2$$

or

$$U_1^2\ U_2^2=\frac{m_2n_2'}{m_1n_1'}$$

or

$$\frac{U_1}{U_2}=\sqrt{\frac{m_2n_2'}{m_1n_1'}}=\sqrt{\frac{M_2}{M_1}}$$

if $n_2'=n_1'=N$ (Avogadro's number).

Further at constant temperature and pressure, the two gases will have the same molar volume.

Hence, $$\frac{U_1}{U_2}=\sqrt{\frac{d_2}{d_1}}$$

where d_1 and d_2 are the densities of gases 1 and 2.

(*e*) **Dalton's Law of Partial Pressure.** If n_1' molecules of a gas, each of mass m_1 and velocity U_1, occupy a volume V, then pressure P_1, exerted by these molecules is given by:

$$P_1=\tfrac{1}{3}\frac{m_1n_1'\ U_1^2}{V} \qquad \ldots (2.34)$$

Similarly, pressure P_2 exerted by n_2' molecules of another gas, each of mass m_2 and velocity U_2 is given by:

$$P_2=\tfrac{1}{3}\ \frac{m_2n_2'\ U_2^2}{V} \qquad \ldots (2.35)$$

In the same manner, pressure P_3 of a third gas is given by:

$$P_3=\tfrac{1}{3}\ \frac{m_3n_3'\ U_3^2}{V} \qquad \ldots (2.36)$$

If all the three gases are forced together in another flask of the same volume and at the same temperature, then total pressure P is given by:

$$P=\tfrac{1}{3}\frac{m_1n_1'U_1^2}{V}+\tfrac{1}{3}\ \frac{m_2n_2'U_2^2}{V}+\tfrac{1}{3}\ \frac{m_3n_3'U_3^2}{V}$$

$$=P_1+P_2+P_3$$

which is Dalton's Law of partial pressure.

The deductions of all these gas laws from the kinetic theory of gases clearly indicate that the equation $PV=\frac{1}{3}\ mn'U^2$ is in agreement with the empirical ideal gas equation, $PV=nRT$

Hence $$PV=\tfrac{1}{3}mn'U^2=nRT$$

Further, since $n'=nN$

where n is the number of moles and N is the Avogadro's number, Hence $PV=\frac{1}{3}\,n(mN)U^2=nRT$

or $$=\frac{nMU^2}{3}=nRT \qquad \ldots (2.37)$$

where $M=Nm$ is the molecular weight of the gas.

Other Deductions from the Kinetic Theory

The Kinetic Energy of Translation. The mean kinetic energy per molecule is given by $\frac{1}{2}\,MU^2$. If n is the number of moles, the total kinetic energy, E_k, of all the molecules is given by:

$$E_k=\tfrac{1}{2}nMU^2$$

or $$E_k=\tfrac{3}{2}\,(\tfrac{1}{3}nMU^2) \qquad \ldots (2.38)$$

From equation (2.37) since $\frac{1}{3}nMU^2=nRT$, equation (2.38) becomes:

$$E_k=\tfrac{3}{2}nRT \qquad \ldots (2.39)$$

and for 1 mole, $E_k=\frac{3}{2}RT$ ... (2.40)

This equation shows that kinetic energy of translational motion is directly proportional to the absolute temperature. This random movement of molecules is called thermal motion of the molecules. When $T=0K(-273.16°C)$, the translational kinetic energy is zero i.e., all the molecular motion stops at absolute zero.

The average kinetic energy per molecule can be obtained from equation (2.40) on its division by Avogadro's number, N, as given below:

$$\frac{E_k}{N}=\frac{3}{2}\;\frac{RT}{N}=\frac{3}{2}kT \qquad \ldots (2.41)$$

where $k=R/N$ is known as the Boltzmann Constant and its numerical value is 1.3805×10^{-16} erg per degree, in SI units its value is 1.3805×10^{-23} JK^{-1}.

Molecular Velocities

Since $PV=\frac{1}{3}nMU^2$

For 1 mole, $PV=\frac{1}{3}\,MU^2$ or $U^2=\frac{3PV}{M}$

Therefore $$U=\sqrt{\frac{3PV}{M}} \qquad \ldots (2.42)$$

From this equation, the velocity of gaseous molecules can be calculated under different conditions as follows:

Since $M/V=d$ (density), equation (2.42) can be written as:

$$U=\sqrt{\frac{3P}{d}} \qquad \ldots (2.43)$$

Again, since $PV=RT$ (for 1 mole), equation (2.43) can also be written as:

$$U=\sqrt{\frac{3RT}{M}} \qquad \ldots (2.44)$$

Thus velocity of gas molecules can be calculated from either of equations (2.42), (2.43) and (2.44) depending upon the data given. If only pressure is given, equation (2.43) is used and when both pressure and density are given, equation (2.43) is used. But if only temperature is given, equation (2.44) is used. To get velocity in cm/sec, pressure should be expressed in dynes/cm^2 and density in grams/c.c. The value of R should be in ergs.

Problem 2.6. Calculate the root mean square velocity of oxygen at N.T.P.

Solution. $U=\sqrt{\frac{3PV}{M}}$

Here $P=1$ atm$=76\times 13.6\times 981$ dynes/cm^2

$V=22{,}400$ c.c., $M=32$

$$U=\sqrt{\frac{3\times 76\times 13.6\times 981\times 22{,}400}{32}}$$

$$=4.6140\times 10^4 \text{ cm/sec.}$$

Problem 2.7. Calculate the root mean square velocity of the molecules of hydrogen at atmospheric pressure. Density of hydrogen is 0.00009 gm/c.c.

Solution. $U=\sqrt{\frac{3P}{d}}$

Here $P=76\times 13.6\times 981$ dynes/cm^2.

$d=0.00009$

$$u=\sqrt{\frac{3\times 76\times 13.6\times 819}{0.00009}}$$

$$=183{,}800 \text{ cm/sec.}$$

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Problem 2.8. Calculate the root mean square velocity of nitrogen at 25°C. The molecular weight of nitrogen is 28.02.

Solution. $U=\sqrt{\frac{3RT}{M}}$

Here $R=8.314\times 10^7$ ergs/deg/mole.

$M=28.02$

$T=298{\cdot}00$

$$U=\sqrt{\frac{3\times 8.314\times 10^7\times 298.00}{28.02}}$$

$$=5.14\times 10^4 \text{ cm/sec.}$$

2.8. THE DISTRIBUTION OF MOLECULAR VELOCITIES

While deducing the equation for pressure from kinetic theory of gases, it was assumed that all molecules are moving with the same speed having root mean square velocity U. But, in actual practice, all the molecules cannot move with the same speed because they are frequently colliding with each other. As a result of this, molecules interchange momentum. Consider, for example, two molecules, with a given velocity and moving in the same direction, collide. It is possible that during collision, one molecule may completely transfer its momentum to the other with the result that the latter molecule will move off with increased velocity and the former may stop completely. It is further possible that latter molecule may again collide with another molecule and attain even higher velocity. The molecules can experience collisions in all the possible directions. Thus, collision results in a redistribution of both energy and velocity. The velocity will vary from zero to very high velocities. Maxwell and Boltzmann, using the theory of probability, have shown that distribution of molecular velocities depends on the temperature and the molecular weight of a gas is given by:

$$\frac{dn_o}{n'}=4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e^{-\frac{MC^2}{2RT}} C^2dC \qquad \ldots (2.45)$$

This equation is known as the Maxwell Boltzmann distribution law. Left hand side of this equation gives the fraction of the total number of molecules, n', having velocities between C and $C+dC$ M is the molecular weight of the gas and T is the absolute temperature. Dividing equation (2.45) by dc we get:

$$1/n' \frac{dn_c}{dc}=4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e^{-\frac{MC^2}{2RT}} C^2 \qquad \ldots (2.46)$$

The left hand side of this equation represents the probability, p, of finding molecules having a particular velocity.

The distribution of molecular velocities can be represented graphically by plotting a curve between probability (p) having various velocities and the velocity C at a definite temperature as shown in Fig. 2.4. The actual curve will depend on the molecular weight of the gas and the absolute temperature, but the general form is always the same.

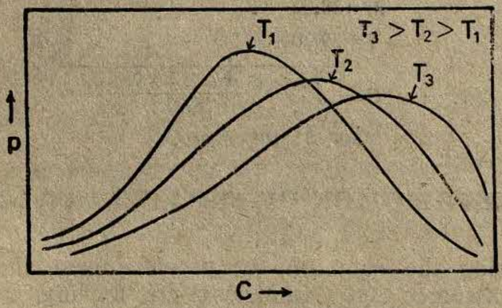


Fig. 2.4. Maxwell's Law of the distribution of molecular velocities.

It can be seen from the diagram that for each curve, p increases with increase of C, passes through a maximum and then begins to decrease. This means that very few molecules possess either very low or very high velocities and majority of the molecules have velocities corresponding to the peak of the curve. The velocity is known as the *most probable velocity*. The most probable velocity in a gas varies with temperature and increases with rise in temperature. Thus when temperature changes from T_1 to T_2, the general form of distribution curve changes from I to II and the maximum shifts to the right indicating that most probable velocity increases with rise in temperature.

It can be shown by mathematical calculations that most probable velocity (C) is given by the expression:

$$C=\sqrt{\frac{2RT}{M}} \qquad \ldots (2.47)$$

The average (or mean) velocity of the molecules of a gas is defined by:

$$V=\frac{C_1+C_2+C_3+\ldots C_n}{n'}$$

and the root mean square velocity, U, as

$$U=\sqrt{\frac{C^2{}_1+C^2{}_2+C^2{}_3+\ldots C^2{}_n}{n'}}$$

where $C_1, C_2, C_3 \ldots C_n$ are the individual velocities of n' molecules in a gas.

It follows from kinetic theory that these velocities are related by the equations:

$$V=0.921\ U$$

and

$$C=\tfrac{2}{3}U$$

On substituting the values of $U=\sqrt{\frac{3RT}{M}}$, we get

$$V=0.921\sqrt{\frac{3RT}{M}}=\sqrt{\frac{8RT}{\pi M}}, \qquad \ldots (2.48)$$

$$C=\sqrt{\frac{2RT}{M}} \qquad \ldots (2.49)$$

and $C:V:U=1:1.128:1.124.$

The marked effect of temperature in increasing the probability of molecules having high velocities or high kinetic energies is due to the presence of the exponential factor $e^{-\frac{MC^2}{2RT}}$ in the Maxwell-Boltzmann distribution equation. Since the quantity $\frac{1}{2}MC^2$ is the kinetic energy. E of a gas/mole having the velocity C, therefore, exponential factor, called Boltzmann factor can be written as $e^{-\frac{E}{2RT}}$.

Since the temperature T is present in the denominator of the negative exponent, this factor will, therefore, remarkably increase with temperature. The greater the temperature, greater is the value of E. Hence, Boltzmann factor rapidly increases with temperature.

Experimental Verification of the Distribution Law

(*i*) **Stern's Method**. This method was first introduced by Stern for the experimental verification of the Distribution Law. The apparatus employed for the purpose consists of a framework as shown in Fig. 2.5. It contains two pairs of slits S_1 and S_2 and there is a platinum filament F coated with silver deposits at the centre. When this is heated electrically, silver atoms evaporate off and those that are able to pass through the slits are deposited on the plates PP. The path of such atoms is along the line PFP. The apparatus is enclosed in an evacuated vessel in order to minimise the collisions between silver atoms. When the whole apparatus is stationary, the silver atoms travel along the line PFP and form a deposit at P. When the framework is rotated rapidly about a vertical axis through F, as shown by the arrows, the direction of movement of the silver atoms is not affected but in the time taken for them to travel from F to P, the latter has moved as a result of the rotation of framework and the apparent path of the atoms is shown by the broken line. Since all the atoms do not have the same speed, the silver deposit is actually spread out in a narrow bond on the plate P instead of being a fine line. The most intense portion is produced by atoms having approximately the average or more exactly, the most probable velocity, thus verifying Maxwell distribution law of velocity.

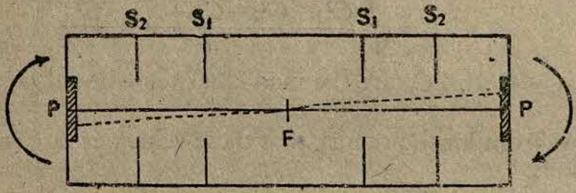


Fig. 2.5. Stern's method.

(*ii*) **Lammert's Velocity Filter Method**. In this method, two toothed discs are mounted at a definite distance apart on a common axle and a beam of molecules, *e.g.*, H_2, N_2, or CCl_4 is arranged as shown in Fig. 2.6. The molecules generated from the source S are passed through a series of slits to get a sharp beam. When the two discs are stationary, the beam passes through the gaps between the teeth on to a radiometer, the deflection of the latter giving a measure of the number of molecules striking it. The discs are then set in rotation. A molecule passing through a gap in the first will pass through a gap in the second only if the time required to travel the distance between the discs is equal to an integral multiple of the time necessary for the discs to rotate from one gap to the next. From a knowledge of the speeds of the discs, therefore, the velocity of the molecules passing through can be determined and the number possessing this velocity is given by the deflection of the radiometer. By changing the velocity of the rotation of the wheels, molecules having different speeds are measured by the radiometer. It is then possible to obtain a velocity distribution curve.

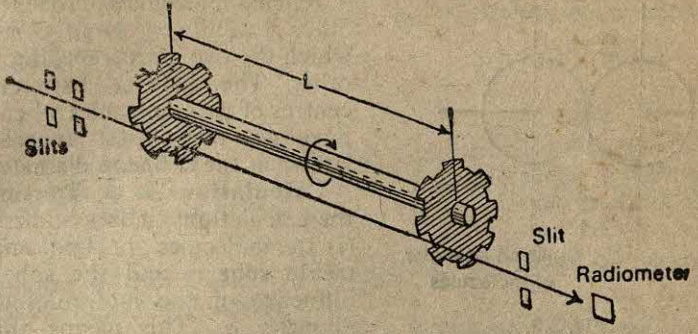


Fig. 2.6. Lammerts' velocity filter method.

2.9. THE MEAN FREE PATH OF GAS MOLECULES

It was pointed out in kinetic theory of gases that molecules of a gas are always in motion and are colliding with each other. The molecules travel in straight line with constant speed until on collision with other molecules, the direction of motion is changed. Thus the path traversed by the molecule is zigzag as shown in Fig. 2.7. The distance that a molecule moves through before colliding with another molecule is known as the free path and the average distance traversed by a molecule between two successive collisions is referred to as the mean free path, A.

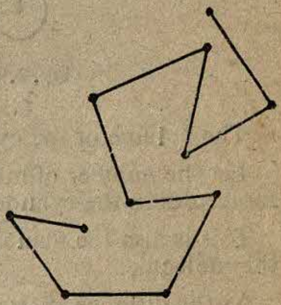


Fig. 2.7. Motion of gas molecules.

If the total path travelled in Z collisions is S, then

$$\lambda = \frac{S}{Z}.$$

The mean free path depends on both the molecular size and the number of molecules because if the molecule is larger in size the number of collisions will be more and mean free path will be shorter. Similarly, larger the number of molecules, smaller is the mean free path.

An expression for the mean free path can be easily deduced from a knowledge of the number of molecules present in a given volume and molecular diameter (frequently known as collision diameter).

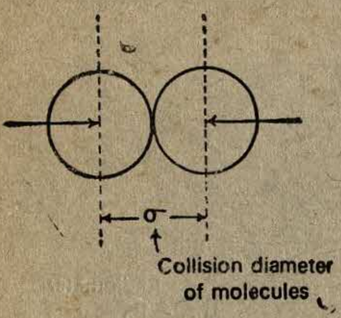


Fig. 2.8.

When a molecule approaches another molecule, a stage comes at which the two start repelling each other. The distance between the centres of two molecules when they have got the closest approach is known as the collision diameter (σ).

Calculation of λ. To simplify the calculations it is assumed that (*i*) the molecules are rigid, impenetrable spheres and the sphere of influence of the molecules has a diameter σ. This means that a molecule can collide only with those molecules, the centres of which lie at a distance σ or less, and (*ii*) only the molecule under consideration is in motion and all others are stationary. Consider a cylinder of radius σ and length C and let C be the velocity of the molecule. Then in one second it will collide with all the molecules the centres of which lie within this cylinder.

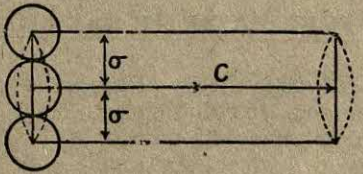


Fig. 2.9. Calculation of mean free path.

The volume of the cylinder$=\pi\sigma^2 C$ . . . (2.50)

Let the number of molecules/c.c. be n'. Then the total number of molecules in the cylinder$=\pi\sigma^2 Cn'$ . . . (2.51)

This is also the number of collisions/second (Z) experienced by the molecule.

As the distance, S, traversed by the molecule in one second is its velocity C, the mean free path is given by:

$$\lambda=\frac{S}{Z}=\frac{C}{\pi\sigma^2.Cn'}=\frac{1}{\pi\sigma^2 n'} \qquad \ldots (2.52)$$

This equation connects the mean free path with the molecular diameter and the number of molecules per unit volume and was deduced by Clausius.

In the deduction of equation (2.52) it was assumed that only one molecule is moving and that all other molecules are stationary. But actually this is not the true picture of a gas because all the molecules are moving in a random manner. Maxwell, utilising his law of distribution of velocities, showed that average speed of the molecules turns out to be $\sqrt{2}C$ and give the following more correct expression for λ.

$$\lambda=\frac{1}{\sqrt{2}\,\pi\sigma^2 n}. \qquad \ldots (2.53)$$

From equation (2.53) it is evident that the mean free path is inversely proportional to the square root of the molecular diameter. Hence smaller is the size of the molecules, the larger will be the mean free path.

Frequency of collisions. The number of collisions per second is known as *collision frequency.*

Since the number of collisions (Z) that a molecule will experience per second with the other molecules is given by:

$$Z=\sqrt{2}\,\pi\sigma^2 Cn' \qquad \ldots (2.54)$$

Therefore, considering similar motion of all the molecules the total number of collisions per second of all the n' molecules/c.c., Z_{11} must be n' times this quantity, *i.e.*,

$$Z_{11}=\sqrt{2}\pi\sigma^2 C(n')^2 \qquad \ldots (2.55)$$

But since each collision involves two molecules, therefore, the number of molecular collisions/c.c./sec. Z_c should be one half this number so that each collision is not counted twice. Therefore,

$$Z_c=\frac{Z_{11}}{2}=\frac{1}{\sqrt{2}}\,\pi\sigma^2 C(n')^2 \qquad \ldots (2.56)$$

If value of $C=\sqrt{\frac{8RT}{\pi M}}$ is substituted into equation (2.56), we get:

$$Z_c=\frac{1}{\sqrt{2}}\,\pi\sigma^2 n'^2\sqrt{\frac{8RT}{\pi M}}$$

or

$$Z_c=2\sigma^2 n'^2\sqrt{\frac{\pi RT}{M}} \qquad \ldots (2.57)$$

All the symbols have the same significance as already discussed.

Problem 2.9. Calculate the number of collisions per second per cubic centimetre at 0°C in hydrogen gas at a pressure of 1.0 atmosphere. The molecular diameter σ for hydrogen is 2.76×10^{-8} cm.

Solution. Since the number of molecules per c.c. is given by

$$n'=Nn=N\frac{PV}{RV}$$

Here $N=6.023\times10^{23}$ molecules/mole

$P=1$ atm, $V=0.0010$ litre

$$R=0.0821 \text{ litre atm/deg/mole}$$

and $$T=273 \text{ K}.$$

Therefore, $$n'=\frac{(6.023\times10^{23})\times1\times0.0010}{0.0821\times273}$$

$$=2.68\times10^{29} \text{ molecules.}$$

The number of collisions per second per cm. Z_c is given by

$$Z_c=2\sigma^2n'^2\sqrt{\frac{\pi RT}{M}}$$

Substituting the various values:

$$Z_c=2\times(2.76\times10^{-8})^2(2.68\times10^{19})^2\sqrt{\frac{3.14\times8.31\times10^7\times273}{2.01}}$$

$$=2.06\times10^{29} \text{ collisions/sec.}$$

2.10. VISCOSITY

This is a property common to both gases and liquids (*i.e.*, fluids) and is a measure of the frictional resistance that a layer of fluid in motion offers to another. Viscosity is produced by the shearing effect of one layer of the fluid moving past another.

Difference in Origin of Viscosity of a Liquid and a Gas

(*a*) **Liquids.** In case of liquids, there are strong attractive cohesive forces between the different molecules. Now, when a layer is moving faster than the other, then due to strong attractive forces, there is slowing down of the faster layer or viscous drag is there.

(*b*) **Gases.** In case of gases, viscosity arises by the jumps of molecules from one layer to the other layer, *i.e.*, transfer of momentum from molecules in one layer to molecules in the other is responsible for viscosity in case of gases. Molecules from faster layer transfer the momentum to molecules of slower layer and try to increase its momentum and vice-versa from slow to faster layer, decrease in the momentum resulting in the formation of a viscous drag.

Relationship between the Mean Free Path and the Viscosity of Gases

The viscosity of gases, which can be accurately determined experimentally, offers a reliable means of estimating the mean free path, as an expression for the viscosity of a gas in terms of the mean free path of its molecules can be deduced on the basis of kinetic theory as follows:

Consider a gas having a laminar flow in the X-direction with a velocity V. The velocity in contact with the surface is zero but increases with increasing distance in the Y-direction. Let dv/dy be the velocity gradient which means that the flow rate increases by an amount dv for every increase of distance dy in the Y-direction. See Fig. 2.10.

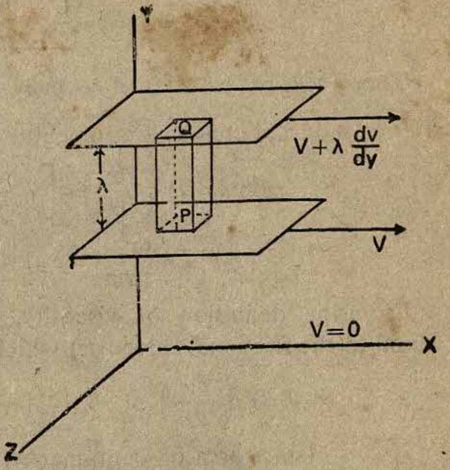


Fig. 2.10. Viscosity of gases.

As a result of continual jump of molecules from one layer to the other, there is a transfer of momentum. Thus if molecules at P which is a slow moving layer jumps to Q—a faster moving layer, it will result in the decrease of momentum and correspondingly the velocity of the molecules in the layer at Q will be decreased. On the other hand, the jump of molecules from Q to P will result in the greater transport of momentum and thus the momentum and velocity of molecules at P will be increased.

In order to simplify the calculations, it is assumed that a molecule experiences a collision only after traversing a distance equal to the mean free path, λ. In other words, it can be said that transfer of momentum takes place only after the molecule has traversed an average distance, λ. Since $\frac{dv}{dy}$ is the velocity gradient, $\lambda\frac{dv}{dy}$ will be the difference in velocity between the two ends of the free path.

If one square centimetre of the area on both the planes is considered and it is assumed that a molecule travels in this area, the excess momentum transported to P layer due to a jump of molecule from Q to P is:

$$=m\left(V+\lambda\frac{dv}{dy}\right)-mV$$

$$=m\lambda\frac{dv}{dy} \qquad \ldots (2.58)$$

where m is the mass of the molecule.

Because of thermal agitation, molecules are moving in all the possible directions. The number of molecules can be divided into three parts parallel to the three coordinate axes. Therefore 1/6 of the molecules will move parallel to any one axis in a particular direction.

If n' be the number of molecules per c.c. having an average velocity C, the number of molecules striking per square centimetre per second upwards or downwards is:

$$=\frac{n'C}{6}$$

Therefore, net transfer of momentum/sec. $=1/6\ mn'\ C\lambda\left(\frac{dv}{dy}\right)$.

Hence the total change in momentum/cm^2/sec.

$$=\tfrac{1}{6}\ mn'C\lambda\left(\frac{dv}{dy}\right)-\left[-\frac{1}{6}mn'\ C\lambda\left(\frac{dv}{dy}\right)\right]$$

$$=\tfrac{1}{3}\ mn'\ C\lambda\frac{dv}{dy} \qquad \ldots (2.59)$$

From the definition of viscosity, this change in momentum is equal to the frictional force (f) which is given by:

$$f=\eta\left(\frac{dv}{dy}\right) \qquad \ldots (2.60)$$

(since area of container $=1$ cm^2)

Equating the equations (2.59) and (2.60), we get

$$\eta\left(\frac{dv}{dy}\right)=\tfrac{1}{3}\ mn'\ C\lambda\left(\frac{dv}{dy}\right)$$

or

$$\eta=\tfrac{1}{3}\ mn'\ C\lambda \qquad \ldots (2.61)$$

But $mn'=\rho$, the density of the gas.

Therefore, $\eta=\tfrac{1}{3}\ \rho\ C\lambda$ ... (2.62)

Equation (2.62) suggests that the measurement of viscosity makes it possible to calculate the value of the mean free path from a knowledge of the density and velocity of the gas.

Again, substituting the value of λ from equation (2.53) into equation (2.61), we get:

$$=\tfrac{1}{3}\ mn'\ C\frac{1}{\sqrt{2}\pi n'\sigma^2}$$

$$=\frac{mC}{3\sqrt{2}\ \pi\sigma^2} \qquad \ldots (2.63)$$

Equation (2.61) can also be written in an other form as follows:

Since $n'=nN$

where n is the number of moles and N, the Avogadro number and $N\times m=M$, the molecular weight of the gas.

Hence, $\eta=\tfrac{1}{3}nMC\lambda$ ... (2.64)

Further, since $C=\sqrt{\frac{8RT}{\pi M}}$ and $\lambda=\frac{1}{\sqrt{2}\pi nN\sigma^2}$

equation (2.64) becomes:

$$=\tfrac{1}{3}\ nM\sqrt{\frac{8RT}{\pi M}}\times\frac{1}{\sqrt{2}\ \pi nN\sigma^2}$$

$$=\frac{2}{3\pi N\sigma^2}\sqrt{\frac{MRT}{\pi}} \qquad \ldots (2.65)$$

Equation (2.65) indicates that the viscosity of a gas is independent of its density. It follows from the reason that at higher density, number of molecules/c.c. are more and thus, λ, the mean free path, is small and transfer of momentum occurs over a small length. If, on the other hand, the number of molecule is small, λ is large and the transfer of momentum takes place over a larger length. Thus the number of molecules and mean free path compensate for each other and hence the viscosity is independent of density.

Another conclusion that follows from equation (2.65) is that the viscosity of a gas is directly proportional to the square root of temperature.

Problem 2.10. The viscosity of hydrogen gas at 0°C is 8.41×10^{-5} poise; determine the mean free path of the molecule at this temperature and 1 atmospheric pressure.

Solution.

$$\eta=\tfrac{1}{3}\rho C\lambda$$

If η is in poise and the density, ρ, in grams, C must be cm/sec.

To determine ρ, since at 0°C and 1 atm., 2.0 grams (1 mole) of hydrogen occupy volume 22,400 c.c., therefore

$$\rho=\frac{2,0}{22,400}=8.9\times10^{-5}\text{ gram/c.c.}$$

Again,

$$C=\sqrt{\frac{8RT}{\pi M}}$$

$$=\sqrt{\frac{8\times8.31\times10^{7}\times273}{3.14\times2.0}}$$

$$=1.70\times10^{5}\text{ cm/sec.}$$

Substituting the values of η, ρ and C in the above equation we get

$$8.41\times10^{-5}=1/3\times8.9\times10^{-5}\times1.70\times10^{5}\times\lambda$$

or

$$\lambda=1.67\times10^{-5}\text{ cm.}$$

2.11. DEGREES OF FREEDOM AND THEIR APPLICATION TO EQUIPARTITION OF ENERGY

The number of degrees of freedom of an object is the number of independent quantities which are necessary to specify in order to describe completely its state or position. For example, in order to define the position of a particle which is free to move in space, all the three axes X, Y and Z of the Cartesian coordinates must be completely known and the particle is said to have three degrees of freedom. Three is the minimum number of coordinates to define a particle in space. Similarly, the number of coordinates required to specify two particles in space are six. If we consider a molecule consisting of N atoms, it will have $3N$ degrees of freedom. But, each atom in a molecule is not capable of moving independently of the other and the molecule executes translational motion as a whole; therefore, translation of the whole molecule can be described in terms of motion of the centre of mass of its constituent atoms. Centre of mass can be considered to be a point in the molecule where the whole mass is concentrated. Now, since three coordinates are essential to define the position of the centre of mass, the number of coordinates required to completely define a molecule comprising of atoms is reduced by three. The remaining $(3N-3)$ degrees of freedom correspond to other modes of motion namely, *vibrational* and *rotational*. These motions are known as internal degrees of freedom and are possessed only by diatomic and polyatomic molecules and not by monoatomic molecules.

The energies possessed by each mode of motion are similar in mathematical form and are expressed as follows:

Translation Kinetic Energy,

$$(E)_{trans}=\tfrac{1}{2}\,mv_x^2 \qquad \ldots (2.66)$$

Rotational Kinetic Energy,

$$(E)_{rot}=\tfrac{1}{2}IW_x^2 \qquad \ldots (2.67)$$

Vibrational Kinetic Energy,

$$(E)_{vib}=\tfrac{1}{2}\mu V^2 \qquad \ldots (2.68)$$

In equations (2.66), (2.67) and (2.68), m is the mass of the molecule, v_x is its velocity in x-direction, I, the moment of inertia chosen about the axis of rotation, W_x, the angular velocity in x direction, μ, the reduced mass of the diatomic molecule defined by $\frac{m_1 m_2}{m_1+m_2}$ (m_1 and m_2 are the masses of atoms) and V, the vibrational velocity of the atoms.

Vibrational potential energy, $(\text{P.E.})_{vib}$ is defined by:

$$(\text{P.E.})_{vib}=\tfrac{1}{2}kx^2 \qquad \ldots (2.69)$$

where x represents the distance of atoms from their equilibrium positions and k is the force constant of the bond.

2.12. LAW OF EQUIPARTITION OF ENERGY ACCORDING TO THE DEGREES OF FREEDOM

It can be shown that the average value of all the energy terms stated above for large number of molecules is same and depends only on temperature. The total energy possessed by molecules of a gas in thermal equilibrium can be distributed equally into translational kinetic energy, rotational kinetic energy, vibrational kinetic energy and vibrational potential energy. This follows from the law of equipartition of energy.

In order to find out the magnitude of the energy possessed by each type of energy, consider the simplest case of translational motion.

Since the velocity in space is related to the component velocities by:

$$U^2=U_x^2+U_y^2+U_z^2$$

Multiplying both sides of this equation by $\tfrac{1}{2}m$ and arranging the squared velocities, we get:

$$\tfrac{1}{2}mU^2=\tfrac{1}{2}mU_x^2+\tfrac{1}{2}mU_y^2+\tfrac{1}{2}mU_z^2 \qquad \ldots (2.70)$$

But $\frac{1}{2}mU^2$ is the total kinetic energy $(E)_T$ of the gas molecules and the terms on the right hand side of equation (2.70) are the average kinetic energies of the molecules resulting from their motion in the x, y and z velocity components and are represented by $(\text{K.E.})_x$, $(\text{K.E.})_y$ and $(\text{K.E.})_z$ respectively.

Therefore, equation (2.70) is written as:

$$(E)_T=(\text{K.E.})_x+(\text{K.E.})_y+(\text{K.E.})_z \qquad \ldots (2.71)$$

But since $(E)_T=\frac{3}{2}kT$ and the velocities in the three directions are equally probable, therefore, each energy term in the particular component will contribute equally to the total energy. Thus, by the principle of equipartition of energy,

$$(\text{K.E.})_x=(\text{K.E.})_y=(\text{K.E.})_z \qquad \ldots (2.72)$$

and

$$(\text{K.E.})_x=\tfrac{1}{2}kT,\ (\text{K.E.})_y=\tfrac{1}{2}kT \text{ and } (\text{K.E.})_z=\tfrac{1}{2}kT \qquad \ldots (2.73)$$

In other words, *the average kinetic energy possessed by the molecules in each component is* $\frac{1}{2}$ *kT per molecule or* $\frac{1}{2}$ *RT per mole.*

This conclusion is also a direct consequence of Boltzmann-Distribution Law.

Similarly, it can be shown that average kinetic energy in vibrational and rotational motion is same and contributes $\frac{1}{2}$ kT to the total energy of the molecules.

2.13. THE SPECIFIC HEATS OF GASES

The specific heat (C) of any substance is defined as the amount of heat in calories required to raise the temperature of one gram of the substance through 1°C. Since in most of the chemical calculations, the quantity considered is 1 mole, the heat capacity is, therefore, referred to as molar heat capacity or as molecular heat. Thus, molecular heat of a substance is the amount of heat required to raise the temperature of a mole of substance by 1°C and is equal to the heat capacity per gram multiplied by the molecular weight of the substance *i.e.*,

Molar heat capacity=Molecular weight × specific heat.

All the substances, particularly gases, have two types of specific heats—one measured at constant volume and the other at constant pressure. If the temperature of a gas is raised at constant volume, the addition of heat will simply increase the internal energy of the gas which is due to the increased kinetic energy of motion of the molecules and no work will be done. This type of heat capacity is known as the *specific heat at constant volume*, C_v. But if a gas is heated at constant pressure, the energy supplied not only increases the internal energy of the gas molecules but also performs some work in the expansion of the gas against the constant external pressure. Heat capacity in this case is referred to as the *specific heat at constant pressure*, C_p. Thus, C_p is always greater than C_v for any gas by the amount of extra heat energy necessary to perform the work of expansion when the temperature of the gas is raised by 1°C. For solids and liquids, the difference between the two heat capacities is very small and negligible because the effect of heat on volume is very small. But in the case of gases, effect of heat on volume is very high. Hence, the difference between the two values of heat capacity is very significant in case of gases.

Application of Kinetic Theory to Specific Heats of Gases. It is supposed that the molecules of a gas possess only one kind of energy, namely, translational energy. As showed earlier, average kinetic energy of translational motion (E_k) of one mole of any ideal gas is 3/2 RT.

E_v is the internal energy of the gas at temperature T. If the temperature is raised by 1°C from T to $T+1$, the internal energy becomes $\frac{3}{2}R\ (T+1)$ and the change in internal energy $\triangle E$, for an increase of temperature of 1°C is given by:

$$\triangle E=\tfrac{3}{2}R\,(T+1)-\tfrac{3}{2}RT$$
$$=\tfrac{3}{2}R \qquad \ldots (2.74)$$

This change in internal energy is equal to the heat capacity per mole at constant volume, C_v, because the heat supplied to 1 mole of gas at constant volume has been used up entirely to raise the translational kinetic energy for 1°C rise in temperature without involving any work.

Therefore, $C_v=3/2\ R$

Since the value of R in calories is 1.987 cal. deg^{-1} mole^{-1}

Therefore, $C_v=3/2\times1.987=2.98$ cal. deg^{-1} mole^{-1} ... (2·75)

Thus, from Kinetic Theory, the molar heat capacity of a gas at constant volume is 2.98 cal. deg^{-1} mole^{-1}.

Now suppose one mole of the gas is heated at constant pressure in a cylinder fitted with a weightless and frictionless piston. The heat supplied will not only increase the translational kinetic energy, as in the case of heating at constant volume, but will also do external work, W, through the expansion it undergoes. The work done W is given by:

$W=P\triangle V$, where $\triangle V$ is the increase in volume due to expansion against the external constant pressure P when the temperature of one mole of gas is raised by 1°C.

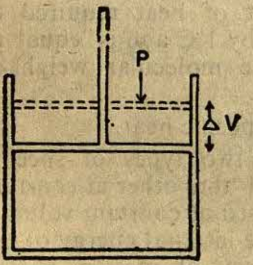


Fig. 2.11. Heat capacity at constant pressure.

Therefore, $C_p=C_v+W$

$$=C_v+P\triangle V \text{ cal deg}^{-1}\text{ mole}^{-1} \qquad \ldots (2.76)$$

But for one mole of an ideal gas, $P\triangle V=R\triangle T$ were $\triangle T$ is the rise in temperature. In this case, as the temperature of the gas has been raised by 1°C; therefore $\triangle T=1$. Hence, $P\triangle V=R$ and equation (2.76) becomes:

$$C_p=C_v+R \text{ cal deg}^{-1} \text{ mole}^{-1} \qquad \ldots (2.77)$$

Thus C_p is greater than C_v by R.

Again since $C_v=3/2R$.

Therefore, $C_p=3/2R+R=5/2R$

$$=5/2\times1.987=4.97 \text{ cal deg}^{-1} \text{ mole}^{-1} \qquad \ldots (2.78)$$

From the above discussion, the following two results are arrived at:

(*i*) The difference between the two heat capacities per mole should be R *i.e.*, $C_p-C_v=R=1.987$ cal deg^{-1} mole^{-1} . . . (2.79) and (*ii*) the ratio of the two heat capacities per mole, C_p/C_v, commonly represented by γ, should be constant equal to $\frac{5}{3}$ *i.e.*,

$$\gamma=\frac{C_p}{C_v}=\frac{\frac{5}{2}R}{\frac{3}{2}R}=\frac{5}{3}=1.667 \qquad \ldots (2.80)$$

It can be seen from the table that only the simple monoatomic gases, such as rare gases, give the values of C_p and C_v as predicted from the Kinetic Theory of gases. On the other hand diatomic gases and all the other gases give larger values than predicted from the Kinetic Theory. But for most of the gases, the difference (C_p-C_v) is approximately equal to 2 cal mole^{-1} deg^{-1}. However, the ratio, γ, goes on decreasing with the complexity of the molecules.

TABLE 2.1

Molar heat capacities for several gases at 15°C (cal deg^{-1} mole^{-1})

Gas	*Formula*	C_p	C_v	C_p-C_v	γ
Helium	He	4.99	3.00	1.99	1.66
Argon	Ar	5.00	3.01	1.99	1.66
Hydrogen	H_2	6.83	4.84	1.99	1.41
Oxygen	O_2	6.96	4.97	1.99	1.40
Chlorine	Cl_2	8.15	6.02	2.13	1.35
Carbon-monoxide	CO	6.94	4.95	1.99	1.40
Carbon-dioxide	CO_2	8.75	6.71	2.04	1.30
Sulphur-dioxide	SO_2	9.71	7.53	2.18	1.29
Ethylene	C_2H_2	10.07	8.01	2.06	1.26
Ethane	C_2H_6	11.60	9.51	2.09	1.22

The usual explanation for the larger values of C_p and C_v is based upon the law of equipartition of energy which has been explained earlier. Since, only in the case of monoatomic gases, the molecules will have kinetic energy of translational motion, therefore, the experimental values of C_p and C_v agree with the theoretical values. But if the gas is diatomic; the molecules, in addition to kinetic energy of translational motion, will have kinetic energy due to vibrational motion and rotational motion. Thus the values of C_p and C_v are larger than the predicted values for diatomic gases. Similar arguments hold for more complex molecules. For the same reason, the ratio of C_p and C_v values for polyatomic molecules goes on decreasing with increasing complexity of the molecules.

Therefore, $\gamma = C_p/C_v = \dfrac{5/2R+E}{3/2R+E} < 1.667$

where E is the energy associated with rotational motion and vibrational motion.

Calculation of Heat Capacities. Consider a monoatomic gas. It has only translational motion. The total energy is given by

$$(\bar{E})_T = \tfrac{3}{2}\,RT$$

and therefore, molar heat capacity at constant volume, for an increase in temperature of one degree.

$$\begin{aligned} C_v &= 3/2R. \\ &= 2.98 \text{ cal/mole K.} \end{aligned}$$

For a diatomic gas or a linear polyatomic molecule, in addition to three translational degrees of freedom, there are two rotational motion and $(3N-5)$ vibrational degrees of freedom. Again, since average energy for each translational and rotational motion is $\frac{1}{2}\,kT$ and for each vibrational motion is kT ($\frac{1}{2}\,kT$ for the kinetic energy $+\frac{1}{2}\,kT$ for the potential energy).

∴ The total average internal energy for one mole of a diatomic gas, say O_2 where $N=2$ is given by

$$\begin{aligned} (\bar{E})_T &= E_{T_r} + E_{rot} + E_{vib} \\ &= \tfrac{3}{2}RT + 2(\tfrac{1}{2}RT) + RT \\ &= \tfrac{7}{2}\,RT \end{aligned}$$

and $\qquad C_v = \frac{7}{2}\,R = 6.93$ cal/mole K.

Similarly it can be shown for a linear triatomic molecule such as CO_2,

$C_v = 10.95$ cal/mole K and for a bent (non-linear) triatomic molecule such as SO_2,

$$C_v = 11.92 \text{ cal/mole K.}$$

The theoretical values of C_v as determined above are found to be higher than the experimental values at 25°C. The reason lies in the fact that at low temperatures, contribution of the vibrational energy to the total energy is not very significant. Thus, if the vibrational energy is subtracted from the total energy at low temperatures, this discrepancy can be removed. As the temperature increases, the contribution due to vibrational energy becomes appreciable and the theoretical values approach experimental values.

The variation of C_v with temperature is contradictory to the simple Kinetic Theory of gases according to which the heat capacity of a gas does not vary with temperature. This is due to the various built-in limitations in the Kinetic Theory which is based on the classical Newtonian mechanics. The quantum mechanical approach, however, provides an explanation for this.

2.14. THE BAROMETRIC FORMULA (VERTICAL DISTRIBUTION)

So far in the discussion of behaviour of ideal gases, it has been assumed that molecules of a gas exert same pressure everywhere in the container and the effect of gravity on the motion of molecules has been considered to be negligibly small. But actually it is not the case, particularly for gases of higher density.

It is an established fact that the density of the air goes on decreasing with increasing height *i.e.*, higher the level, lower is the pressure.

To understand it, consider a cylinder placed in a vertical position containing a gas, the molecules of which are subjected to a gravitational force, the only external force acting downward. The temperature of the gas is kept constant.

In order to find out the pressure of the gas in the column at any height, it is necessary to determine the total weight of the gas in the column above that height. Now, since weight is a force, therefore, force per unit area gives the pressure.

Consider a thin layer of gas of thickness *dz* and cross-sectional area 1 cm² at a height *Z*.

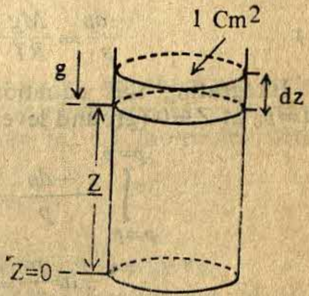


Fig. 2.12. Column of a gas in a gravity field.

Let p be the pressure at a height Z and $(p-dp)$ the pressure at a height $(Z+dz)$. The negative sign indicates that as the height increases, the pressure decreases.

Weight of the layer acting downward

$$= \text{mass} \times \text{acceleration due to gravity}$$

$$= dz \times 1 \times \rho \times g \qquad \ldots (2.81)$$

(since mass=volume × density and volume=$dz \times 1$)

where ρ is the density of the gas.

If $\frac{-dp}{dz}$ is the pressure gradient, the difference in pressure between the two heights of the layer is

$$= \frac{-dp}{dz}\,(Z+dz) = -Z\left(\frac{-dp}{dz}\right)$$

$$= -dp \qquad \ldots (2.82)$$

This difference is equal to the weight of the layer between these two heights, the cross-sectional area of which is 1 cm^2.

Thus $$-dp = \rho g dz \qquad \ldots (2.83)$$

This equation indicates that the change in pressure is directly proportional to the density of the gas and the negative sign explains that the pressure decreases as the height increases.

If the gas is ideal, its density (ρ) is determined as follows:

Since $\rho = M/V$ where M is molecular weight of the gas and V is the volume,

and $$V = \frac{RT}{p} \qquad \text{(Ideal gas equation, } pV=RT\text{)}$$

Hence $$\rho = \frac{Mp}{RT}$$

Therefore, equation (2.83) becomes:

$$-dp = \frac{Mg}{RT}\,.\,pdz$$

r $$\frac{-dp}{p} = \frac{Mg}{RT}\,.\,dz \qquad \ldots (2.84)$$

Integrating this equation between the limits $p=p$ at height Z and $p=p_0$ at $Z=0$ (ground level), we get

$$\int_{p=p_0}^{p=p} \frac{-dp}{p} = \frac{Mg}{RT}\int_{Z=0}^{Z=Z} dz$$

$$-ln\frac{p}{p_0} = \frac{MgZ}{RT}$$

or $$p = p_0 e^{-\frac{MgZ}{RT}} \qquad \ldots (2.85)$$

Since the density is proportional to pressure and the number of particles per cubic centimetre is also proportional to the pressure, equation (2.85) can also be written in the two other forms:

$$p = p_0 \cdot e^{-\frac{MgZ}{RT}} \qquad \ldots (2.86)$$

and $$n = n_0\, e^{-\frac{MgZ}{RT}} \qquad \ldots (2.87)$$

where ρ and ρ_0 are the densities and n and n_0 are the number of particles per cubic centimetre at height Z and at ground level ($Z=0$).

Any of the equations (2.85), (2.86) or (2.87) is an expression of the Barometric distribution law or the gravitational distribution law as it explains the distribution of the gas in a column extending upward into the atmosphere.

Deduction of Boltzmann Distribution Law. This can be easily done from equation (2.87) as given below:

Since gravitational potential energy per mole at a height Z is given by $E_p=MgZ$.

Therefore, equation (2.87) becomes:

$$n=n_0\,e^{-\frac{E_p}{RT}} \qquad \ldots (2.88)$$

In the potential energy of the individual molecule, say ϵ_p, is considered, then

$$n=n_0\,e^{-\varepsilon_p/kT} \qquad \ldots (2.89)$$

Where k is a constant per molecule and is known as the Boltzmann constant.

Equation (2.89) is a special case of the general law deduced by Boltzmann in 1886. With the help of this equation, it is possible to find the number of molecules (n) in any state in terms of potential energy of that state. Thus if n_x is the number of particles in any state where potential energy is ϵ_x, then:

$$n_x=n_0\,e^{-\frac{\varepsilon_x}{kT}}$$

The energy will be different for different states. But there are some special cases where several different states may have the same energy. If g_x states have the same energy ϵ_x, the number of molecules with energy ϵ_x is given by:

$$n_x=g_x n_0\,e^{-\frac{\epsilon_x}{kT}}$$

g_x is known as the degeneracy of the level with energy ϵ_x.

Boltzmann relation can also be expressed as a fraction out of the total number of molecules in a gas having energy ϵ_x.

Since the total number of molecules is given by

$$n'=\Sigma n_x=n_0\Sigma g_x\,e^{-\frac{\epsilon_x}{kT}}$$

the required fraction is

$$\frac{n_x}{n'}=\frac{g_x n_0\,e^{-\frac{\epsilon_x}{kT}}}{n_0\Sigma g_x\,e^{-\frac{\epsilon_x}{kT}}}$$

$$\frac{n_x}{n'}=\frac{g_x\,e^{-\frac{\epsilon_x}{kT}}}{\Sigma g_x\,e^{-\frac{\epsilon_x}{kT}}}$$

or
$$\frac{n_x}{n'}=\frac{g_x}{f}.e^{-\frac{\epsilon_x}{kT}} \quad \ldots (2.90)$$

where the quantity f is called the partition function or sum over states.

Problem 2.11. Calculate the weight of air in a column of 1 cm² in area and arising from sea level to an altitude of 1.5×10^6 cm (about 10 miles), allowing for the barometric decrease in pressure. Assume air to be a uniform gas of molecular weight 29 and a uniform temperature of 0°C. The atmospheric pressure is equal to the total weight of gas in a column of unit area and of infinite height.

Solution. The pressure at this altitude is given by the barometric equation as:

$$\text{Log } p/p_0=\frac{-MgZ}{2.303\;RT}$$

Substituting the various values:

$$\text{Log } \frac{p}{1}=-\frac{29\times981\times1.5\times10^6}{2.303\times8.31\times10^7\times273}$$

or
$$p=0.152 \text{ atm}.$$

Again 1 atm. $=760$ mm Hg$=1\times10^6$ dynes/cm².

Since the weight of the full column of air extending down to sea level is 10^6 dynes/cm², the weight extending down only to the given altitude will be 0.150×10^6 dynes/cm².

2.15. REAL GASES

Deviations from ideal behaviour. A gas is said to be an ideal gas if it obeys the various gas laws, expressed in the form of equation $PV=nRT$. On studying the actual behaviour of various gases, it is found that very few gases obey the ideal gas equation only at low pressures and high temperatures. However, at high pressures and low temperatures, marked deviations from the ideal behaviour have been observed. To illustrate how much a gas deviates from ideal gas behaviour, consider the expression $PV=nRT$. At constant temperature, this equation reduces to $PV=$constant, which is Boyle's Law. In words, the product of pressure and volume for a definite quantity of various gases at constant temperature should remain constant at all pressures.

Figure 2.13 shows a plot of PV versus P for various gases at 0°C. For an ideal gas, the plot should be a straight line parallel to the abscissa. Such a plot is indicated by the dotted line. It is obvious from the various plots that all gases deviate considerably from the ideal gas behaviour and the product PV does not remain constant with increasing pressure. Only in the limit of zero pressure, all gases are behaving ideally.

A close examination of the Fig. 2.13 reveals the fact that all the curves can be classified into two types:

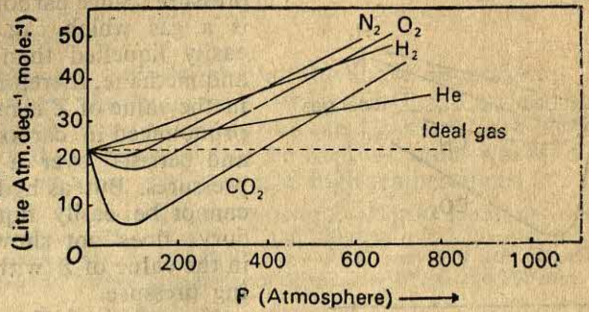


Fig. 2.13. *PV* vs *P* plot for various gases at 0°C.

Type One. Here the curve starts ascending at once from the value of *PV* and the value of *PV* increases continually with increasing pressure. This type of curve is obtained for various gases having smaller molecules, *e.g.*, H_2, He, etc.

Type Two. Here the curve starts again at the value of *PV*, shows a decrease in *PV* in the beginning, passes through a minimum and then begins to increase with increasing pressure. This type of curve is generally obtained for gases having larger molecules, *e.g.*, O_2, CO_2 etc.

To show both the deviations more clearly, a quantity, called compressibility factor (*Z*) is employed which is defined as:

$$Z=\frac{PV}{RT}$$

where *V* is the volume occupied by one mole of the gas at a given temperature *T* and pressure *P*.

For an ideal gas, $Z=1$ and is independent of pressure and temperature.

For real gases, *Z* is a function of both temperature and pressure and its value varies. The amount by which the actual factor differs from a value of unity gives a measure of deviation from the ideal behaviour.

Again, since $(PV)_{ideal}=RT$

Therefore, $$Z=\frac{PV}{RT}=\frac{PV}{(PV)_{ideal}}$$

Hence compressibility factor is an index of deviation from ideality.

Figure 2.14 shows a plot of *Z* versus *P* for some gases at 0°C. For H_2, the value of *Z* continually increases but for N_2, CH_4 and CO_2, *Z* first decreases and then increases quite rapidly with increasing pressure.

It has been found that for those gases which can easily be liquefied, Z decreases sharply below the value of unity at low pressure. Since carbon dioxide is a gas which can be more easily liquefied than nitrogen and methane, therefore, the dip in the value of Z is much more pronounced in carbon dioxide and persists over a range of pressures. But as hydrogen gas cannot be easily liquefied, its curve does not show any dip in the value of Z with increasing pressure.

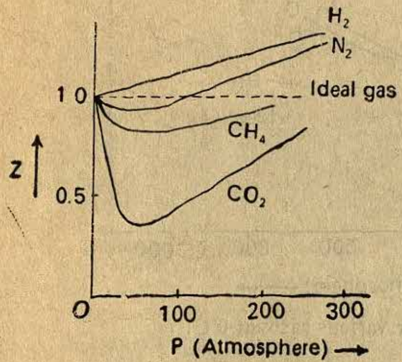


Fig. 2.14. Z versus P curves for various gases at 0°C.

If a plot of Z versus P is constructed for a gas at several temperatures, it is found that as the temperature decreases, the dip in the curve is more pronounced.

Figure 2.15 shows various curves of Z versus P for nitrogen at various temperatures. All the curves start with $Z=1$ at $P=0$ and value of Z varies from unity as pressure increases in a manner dependent on temperature. As the temperature increases, the minimum in the curve becomes smaller and shifts towards lower pressures. However, a temperature is reached at which Z remains close to unity over an appreciable range of pressures. In this case, this temperature is 50°C. The temperature at which this takes place is called the *Boyle temperature* or *Boyle point* and is characteristic for the gas. For every gas when the temperature is below the Boyle temperature, the value of Z will first decrease with increasing pressure, pass through a minimum and then increase continuously. But if the gas is above

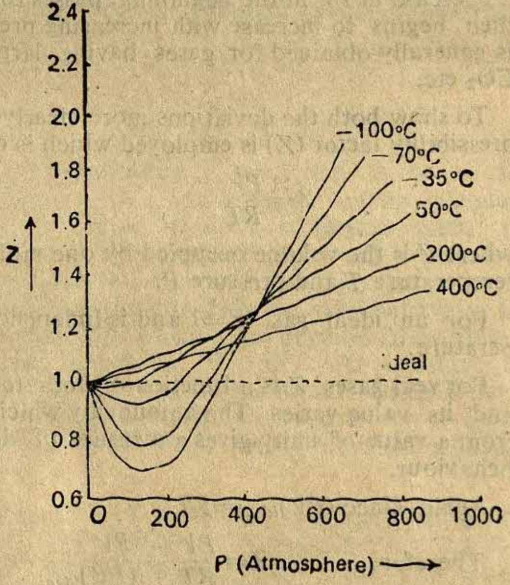


Fig. 2.15. Compressibility factors for nitrogen at various temperatures.

the Boyle point, Z increases sharply with increasing pressure and the values of Z are higher than unity.

Similarly deviations from Gay-Lussac's Law and Avogadro's Law are also observed.

Thus taking into consideration all the above discussion, it can be said that when the pressure is very small (1 atm or less) and temperature is high, the deviations from ideal gas laws are very small and the ideal gas equation may be used. In other words, a gas behaves ideally at lower pressures and high temperatures.

Problem 2.12. The compressibility factor $Z=PV/nRT$ for N_2 at $-50°C$ and 800 atm pressure is 1.95; and at 100°C and 200 atm, it is 1.10. A certain mass of nitrogen occupied a volume of 1.00 litre at $-50°C$ and 800 atm. Calculate the volume occupied by the same quantity of nitrogen at 100°C and 200 atm.

Solution. $Z_1=\frac{P_1V_1}{nRT_1}$ at temperature T_1, volume V_1 and pressure P_1

Similarly, $Z_2=\frac{P_2V_2}{nRT_2}$ at temperature T_2, volume V_2 and pressure P_2

$$n=\frac{P_1V_1}{RT_1Z_1}=\frac{P_2V_2}{RT_2Z_2}$$

or

$$V_2=\frac{P_1V_1}{P_2}\cdot\frac{Z_2T_2}{Z_1T_1}$$

$$=\frac{800\times1.00\times1.10\times373.2}{200\times1.95\times223.2}$$

$$=3.77 \text{ litres.}$$

2.16. CAUSES OF DEVIATIONS

It has been shown that gases do not obey the various gas laws and exhibit remarkable deviation from ideality particularly at low temperatures and high pressures. The reason for deviation lies in the fact that in the discussion of Kinetic Theory of gases, it was assumed that the volume occupied by the gas molecules is negligibly small as compared to the total volume of the gas and molecules do not exert any force of attraction on each other. But in reality, both these assumptions are wrong as proved below.

"Molecules of the gas do occupy some volume" can be established from the fact that the molecules have collision diameter which can be possible only if the molecules have a finite volume.

Further, when the temperature of the gas is decreased and pressure is increased, a stage is reached where the molecules of the gas are so close that the liquefaction and finally the solidification of the gas takes place. Solid cannot be further compressed. This confirms that molecules of the gas occupy some volume. Again, liquefaction of the gas is possible only if there are forces of attraction between the molecules. Although these forces are much larger in liquids but nevertheless they are not negligible in gases. This is also confirmed by the Joule-Thomson effect according to which when a gas at constant pressure is passed through a porous plug, it suffers a decrease in temperature and hence in kinetic energy.

Thus these two assumptions must be modified before they are applicable to real gases.

2.17. MODIFICATION OF THE IDEAL GAS EQUATION

The van der Waals Equation. The first attempt to incorporate the finite volume of the molecules of the gases and attractive forces between them into ideal gas equation was made by van der Waals in the year 1873. He made an allowance for both factors and gave an equation known after his name.

Correction for the finite volume of the molecules. Since the molecules of the gas occupy some volume, therefore, space in which the molecules can move is less than the total volume of the gas by an amount equal to the finite volume of the molecules. Thus, the volume occupied by the molecules should be subtracted from the total volume of the gas in order to get the ideal volume.

If b is the volume occupied by molecules in one mole of a gas, then the volume occupied by n moles of the gas molecules is nb. This is known as the excluded volume. Hence the ideal volume, V_i, is given by

$$V_i=(V-nb) \qquad \ldots (2.91)$$

The factor b is not equal to the actual volume of the molecules but it is four time equal to the actual volume of the molecules. This can easily be shown by considering two molecules approaching each other. If σ is the diameter of each molecule, the molecules cannot approach more closely than the distance σ as they are impenetrable. Within a sphere of radius σ $(=2r)$, no volume will be occupied by this pair of molecules.

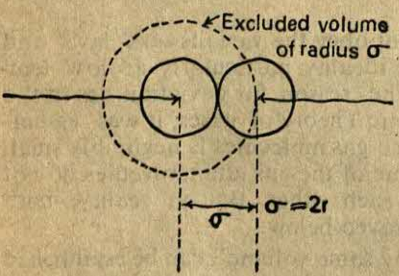


Fig. 2.16. Volume correction.

Thus, the excluded volume per pair of molecules

$$=\tfrac{4}{3}\pi\,(2r)^3=8(\tfrac{4}{3}\pi r^3)$$

and for a single molecule, excluded volume is:

$$=\tfrac{1}{2}(8)\,(\tfrac{4}{3}\pi r^2)=4(\tfrac{4}{3}\pi r^3)$$

$$=4V_m.$$

where V_m is the volume of a single molecule.

Correction for the attractive forces operating between the

molecules. A molecule within the interior of the gas is surrounded by other molecules equally in all directions and thus the net force of attraction on it is zero. However, when it approaches the wall of the container, the uniform distribution of the molecules about this molecule is upset and it will be subjected by molecular attraction to an inward pull as there is no molecule on the other side. Due to this one sided molecular attraction, the force with which the molecule strikes the wall will be less than the force if there were no inward pull. Consequently the measured pressure, P, is less than the ideal pressure, P_i, by an amount say P' *i.e.*,

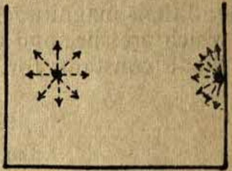


Fig. 2.17. Pressure correction.

$$P=P_i-P'$$

or
$$P_i=P+P'$$

In other words, it is necessary to add a correction term to the actual pressure in order to get the ideal pressure.

Now, the force of attraction exerted on a molecule when it is going to strike the wall is directly proportional to the number of molecules per unit volume in the body of the gas. Again, the number of molecules striking the wall is also proportional to the number of molecules per unit volume of the gas.

If V is the volume occupied by n moles of the gas, then both these two factors and hence the correction term, P', is directly proportional to $\frac{n^2}{V^2}$.

i.e.
$$P'\propto\frac{n^2}{V^2}$$

or
$$P'=\frac{n^2a}{V^2}$$

where a is a constant characteristic of each gas.

Thus the ideal pressure,

$$P_i=P+\frac{n^2a}{V^2} \quad \text{. . . (2.92)}$$

The product of ideal pressure and ideal volume indicated by equations (2.92) and (2.91) respectively should be equal to nRT *i.e.*,

$$\left(P+\frac{n^2a}{V^2}\right)(V-nb)=nRT \quad \text{. . . (2.93)}$$

This is known as the van der Waals equation for n moles of a gas.

For 1 mole of a gas, van der Waals equation becomes:

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT \quad \text{. . . (2.94)}$$

The constants *a* and *b* are known as the van der Waals constants and their magnitudes depend on the type of the gas and the units in which pressure and volume are expressed. The values of the van der Waals constants for some gases are given in Table 2.2.

TABLE 2.2.

van der Waals constants for some gases

Gas	$a/dm^6\ atm\ mol^{-2}$	$100\ b/dm^1\ mol^{-3}$
He	0.0341	2.370
Ne	0.2107	1.709
Ar	1.345	3.219
Kr	2.318	3.978
Xe	4.194	5.105
H_2	0.244	2.661
O_2	1.360	3.183
N_2	1.390	3.913
CO_2	3.592	4.267
H_2O	5.464	3.049
NH_3	4.170	3.707

Problem 2.13. Calculate the pressure exerted by 1 mole of water vapor in 20 litres at 27°C, using (*a*) the ideal gas law (*b*) van der Waals equation. The values of van der Waals constants *a* and *b* for water vapor are 5.464 $litre^2$ atm. $mole^{-2}$ and 0.03049 litre $mole^{-1}$ respectively.

Solution. (*a*) $P=\frac{RT}{V}$

$$=\frac{(0.08205\ \text{litre atm deg}^{-1}\ \text{mole}^{-1})\ (300\ \text{deg})}{20.00\ \text{litre mole}^{-1}}$$

$=1.23$ atm.

(*b*) $P=\frac{RT}{V-b}-\frac{a}{V^2}$

$$=\frac{(0.08205\ \text{litre atm deg}^{-1}\ \text{mole}^{-1})\ (300\ \text{deg})}{(20-0.03049)}$$

$$-\frac{5.464}{400\ \text{litre}^2\ \text{mole}^{-2}}$$

$=1.218$ atm.

2.18. EXPLANATION OF BEHAVIOUR OF REAL GASES FROM van der Waals EQUATION

van der Waals equation can explain the behaviour of real gases up to some extent although not completely as shown below:

$$PV=RT+Pb-a/V+ab/V^2 \qquad \ldots (2.95)$$

(*i*) **At low pressure.** When P is small, V will be large and, therefore, terms Pb and ab/V^2 are negligible in comparison to a/V (b i also very small in comparison to V). Hence, equation (2.95) reduces to:

$$PV=RT-a/V.$$

Thus, when the pressure is low, the product PV is smaller than RT by an amount equal to a/V. When P increases, V decreases or a/V increases and, therefore, PV will go on decreasing. This explains the dip in the plot of PV versus P curves for CO_2 and O_2 in Fig. 2.13.

(*ii*) **At high pressure**. When P is high, V will be small. Now the terms a/V and ab/V^2, which have opposite signs and approximately the same magnitude, are negligibly small in comparison to the other two terms in the right hand side of equation (2.95).

Thus equation (2.95) reduces to P

$$PV=RT+Pb.$$

Therefore, when pressure is high, the product PV is greater than RT by an amount equal to Pb and that increases linearly with increase of P.

This explains why at high pressures, the product PV is always greater than the desired value for all gases as shown in Fig. 2.13.

(*iii*) **At extremely low pressures and high temperatures.** When P is very small, V will be very large. In this case, both the correction terms a/V^2 and b, in the van der Waal's equation are negligibly small in comparison to P and V and the equation reduces to $PV=RT$, the equation for an ideal gas. Similarly, when the temperature is very high, V will be very large (since volume $\propto$ temperature) or P will be very small and again the equation, $PV=RT$ is obtained. Thus at extremely low pressures and high temperatures, all real gases obey the ideal gas laws.

(*iv*) **Exceptional behaviour of hydrogen and rare gases.** Since for such gases, the attractive forces between the molecules are very small; the values of a are, therefore, found to be very small. Hence the term a/V^2, the effect of which is predominant at low pressure, is negligible. However, the effect of b, the volume of the molecules, predominates even at low pressure and so the van der Waals equation reduces to $P(V-b)=RT$ or $PV=RT+Pb$.

In words, for gases like H_2, He etc., the product PV is always higher than RT by an amount equal to Pb.

This explains the reason why the product PV for hydrogen and helium, as shown in Fig. 2.13, begins to increase sharply with increase of pressure.

2.19. OTHER EQUATIONS OF STATE

A large number of other equations have been suggested to represent $P-V-T$ relations of the gases more satisfactorily. Some of them are empirical and some are theoretical. Some important questions of state are given below:

Dieterici Equation. This equation makes an allowance for the forces of attraction on molecules and its effect on the pressure. The equation is:

$$P(V-b)=RT\ e^{-a/RT}$$

where e is the base of natural logarithms.

This equation agrees with the van der Waals equation over small ranges of pressure. At high pressure, the two equations differ considerably and Dieterici equation gives results which are more in agreement with the experimental results.

Clausius Equation. Clausius showed that the factor a in the van der Waals equation is not independent of temperature and used the term $\dfrac{a}{T(V+c)^2}$ for a/V^2. The proposed equation is:

$$\left[P+\frac{a}{T(V+c)^2}\right](V-b)=RT$$

where c is some constant.

This equation explains $P-V-T$ relations fairly well for some gases and not for all gases.

Dieterici Equation. This equation makes an allowance for the forces of attraction on molecules and its effect on the pressure. The equation is:

$$P=\left(\frac{RT}{V}-b\right)\exp.\left(-\frac{a}{RTV}\right) \qquad \ldots (2.96)$$

Using this equation the values of critical constants are given as under:

$$P_c=\frac{a}{4e^2b^2}\,;\ V_c=2b;\ T_c=\frac{a}{4bR} \qquad \ldots (2.97)$$

$$Z_c=\frac{2}{e^2}=0.2706$$

Dieterici equation gives results which are more in agreement with the experimental results.

Berthelot Equation. The equation is of the form,

$$P=\frac{RT}{V-b}-\frac{a}{TV^2} \qquad \ldots (2.98)$$

Using this equation the values of the critical constants are found to be

$$P_c=\frac{1}{12}\left(\frac{2aR}{3b^3}\right)^{1/2};\ V_c=3b \qquad \ldots (2.99)$$

$$T_c=\frac{2}{3}\left(\frac{2a}{3bR}\right)^{1/2};\ Z_c=\frac{3}{8}=0.375$$

Beatie-Bridgeman Equation. The equation is of the form,

$$P=\frac{(1-\gamma)RT(V+\beta)}{V^2-\dfrac{\alpha}{V^2}} \qquad \ldots (2.100)$$

$$\alpha=\alpha_0\left(1+\frac{a}{V}\right)$$

$$\beta=b_0\left(1-\frac{b}{V}\right)$$

$$\gamma_0=\frac{c_0}{VT^3} \qquad \ldots (2.101)$$

The Kamerlingh Onnes Equation. This is an empirical equation and gives PV as a power series of the pressure at any given temperature. This equation is written as:

$$PV_m=A+BP+CP^2+DP^3+\ldots$$

P is the pressure and V_m is the molar volume. The coefficients A, B. C, D etc., are known respectively as the 1st, 2nd, 3rd, 4th etc. *virial coefficients*. When the pressure is very low, only the 1st coefficient A, equal to RT, is significant and others are neglected. When the pressure is high, the other coefficients are also significant and are taken into consideration. The order of significance of these coefficients is their order in the equation. The values of all these coefficients, although constant at a given temperature, vary with temperature.

This equation can be made to explain the experimental results with fair accuracy.

PROBLEMS

1. Explain the expressions:

$$PV=K,\quad P=\frac{K}{V},\quad V=\frac{K}{P}.$$

What is the meaning of K?

2. What is the pressure in atm. if the difference in the levels of Hg in an open end manometer is 76 cm? 500 mm? The atmospheric pressure is 74.0 cm. Hg.
Ans. 0.053 atm. 0.316 atm.

3. A mixture consists of 0.495 gram of gas A of molecular weight 66.0 and 0.182 gram of a gas B of molecular weight 45.5; the total pressure is 76 2 cm of mercury. Calculate the partial pressures of the two gases.
Ans. 49.7 and 26.5 cm of mercury.

4. Using the ideal gas, with P and V expressed in proper C.G.S. units, calculate the value of R (*a*) in ergs per degree per mole, (*b*) litre-atm per degree per mole, (*c*) cals per degree per mole.

5. Calculate the number of (*a*) ergs per molecule, (*b*) Kcal per mole corresponding to one electron volt per molecule. The electron volt is energy acquired by an electron in falling through a potential difference of one volt,
Ans. (*a*) 1.6×10^{-12} (*b*) 23.05

6. At 27°C, 500 cc. of H_2 measured under a pressure 400 mm Hg and 1000 c.c. of N_2, measured under a pressure of 600 mm Hg are introduced into an evacuated flask of 2-litre capacity. Calculate the resulting pressure in mm of mercury.
Ans, 400 mm Hg

7. Comment on the postulates of kinetic theory of gases. Derive the expression for the pressure exerted by one mole of an ideal gas.

8. Write explanatory notes on:
    (*a*) Root mean square velocity.
    (*b*) Most probable velocity.
    (*c*) Average velocity.
    (*d*) Mean free path.

9. Explain in terms of kinetic molecular theory:
    (*a*) High compressibility of gases.
    (*b*) Pressure exerted by a gas.
    (*c*) Temperature of a gas.
    (*d*) Dalton's law of partial pressure.

10. Deduce gas laws from the kinetic theory of gases. Calculate the pressure exerted by 10 g of nitrogen enclosed in a 1-litre vessel at 25°C. Assume that nitrogen behaves ideally. **Ans.** 8.73 atm.

11. (*a*) Calculate the root mean square velocity and average velocity of CO_2 molecules at 18°C and 400 mm pressure. **Ans.** 48390 cm/sec. 40620 cm/sec.

(*b*) The density of hydrogen at 0°C and 760 mm pressure is 0.00009 g/ml. Calculate r.m.s. velocity of hydrogen molecules (density of Hg=13.6 gm/cc.) **Ans.** 183900 cm/sec.

12. Calculate the average, most probable and the root mean square velocity of O_2 molecules at 25°C. At what temperature would hydrogen have the same values of velocities?

Ans. 3.2×10^4 cm/sec; 2.8×10^4 cm/sec. 4.7×10^4 cm/sec.

13. What is the mean free path of Argon at 25°C and a pressure of 1 atm; given $d=2.86$ A. **Ans.** $\lambda=1115$ Å

14. (*a*) Derive the barometric formula.

(*b*) The gravitational constant *g* decreases by 1.0 cm/sec^2 km of altitude. Assuming a constant temperature of 25°C, derived a modified barometric equation that recognizes this variation in *g*. Calculate the pressure of nitrogen at 300 km altitude taking sea-level pressure to be 1 atm and using this modified equation. **Ans.** 6.4×10^{-13} atm.

15. (*a*) Starting from the kinetic gas equation, calculate the ratio of the specific heats at constant pressure (C_p) and at constant volume (C_v) in the case of a mono atomic gas.

(*b*) How does the ratio C_p/C_v vary with the molecular complexity of a gas?

(*c*) The equi-partition value of γ, (C_p/C_v) for ozone is 1.15. Assuming ideal gas behaviour, is the molecule linear or non-linear?

16. Derive the Maxwell-Boltzmann Distribution Law. Give a method for its experimental verification.

17. Write notes on the following:
    (*a*) Viscosity of gases.
    (*b*) Degrees of freedom.
    (*c*) Law of Equipartition of Energy.

18. Comment on the following statements: (*a*) The fact that molecules attract one another cause a gas to deviate from ideal behaviour.

(*b*) The fact that the actual volume occupied by molecules is not negligible cause a gas to deviate from ideal behaviour.

(*c*) The molecular attraction between the gas molecules is high at low temperatures.

19. (*a*) Derive van der Waals' equation for n moles of a real gas. What is the effect of temperature on the van der Waals' constants a and b?

(*b*) Show that b, the co-volume, is equal to four times the actual volume of the molecule.

20. One molecule of carbon monoxide has a volume 1.5 litres at a temperature of 27°C. If R is taken in litre atmospheres, then the values of 'a' and 'b' are 1.05 and 0.04 respectively. Find the pressure of this gas using van der Waals' equation.

(*b*) van der Waals' constant 'b' for O_2 gas is 0.0318 litres moles^{-1}. Calculate the diameter of the oxygen molecules. Ans. 2.934×10^{-8} cm.

Chapter 3

LIQUIDS

3.1. LIQUIDS AND THE CRITICAL PHENOMENA

It was pointed out in the chapter on gases that liquids differ from gases in terms of the intermolecular forces and the mean free path of the constituent particles. The intermolecular forces in gases are very small and the gas molecules have got free existence. That is why the molecules of a gas are in a state of constant rapid motion moving in all the possible directions. The mean free path is also very much larger than the molecular diameter.

Liquids are characterised by strong cohesive forces and these forces do not permit the molecules to have translational motion as freely as in a gas. Thus for a liquid, the molecules have restricted motion and the mean free path is much shorter than in the gas phase.

Every gas can be converted into liquid state by decrease of temperature and increase of pressure. However, the effect of temperature is more predominant than that of pressure because for every gas, there is a temperature above which it cannot be liquefied howsoever high pressure is applied. This temperature above which a gas cannot be liquefied and below which a continuous increase of pressure will ultimately result in the liquefaction of the gas is referred to as the *critical temperature.* The pressure required to liquefy the gas at the critical temperature is known as the *critical pressure* and the volume occupied by one mole of the gas at critical temperature and pressure is called the *critical volume.* Critical temperature, critical volume and critical pressure of a gas are together known as the *critical constants* of a gas.

The critical phenomena is reversible.

The critical phenomena was first studied in detail by Andrews in 1869, when he determined the isotherms (curves between pressure and volume at constant temperature) of carbon dioxide at different temperatures. The results are shown in Fig. 3.1.

At 48.1 °C, the curve is a hyperbola as is obtained in the case of an ideal gas. Same is the result at 35.5°C but here, there is some deviation from the correct form. At 30.98°C, the isotherm shows a marked deviation from the ideal gas behaviour. This curve remains horizontal for a short period and at the point *X*, a great decrease of volume is indicated for a small change of pressure. Also at *X*, liquid is observed for the first time. At still lower temperatures, the horizontal portions of the curves are much more pronounced. Lower the temperature, larger is the horizontal portion. Consider the isotherm *ABCD* at 13.1°C. The portion *AB* represents the compression of CO_2 gas. At *B*, the liquefaction commences and the curve *BC* remains horizontal thus indicating a great decrease of volume at constant pressure. Along this line, the gas is changing into liquid. At *C*, the liquefaction is complete. Further increase of pressure from *C* to *D* results in a slight decrease of volume since liquids cannot be easily compressed. Thus, the portion *CD* of the curve is almost vertical. It should be noted that along *AB*, only gas exists and along *CD*, only liquid exists while along *BC*, both gas and liquid are existing together. At a somewhat higher temperature say at 21.5°C, the behaviour is qualitatively same except that the horizontal portion, over which liquefaction takes place, is smaller. If the temperature is increased further, horizontal portion becomes smaller and smaller till it shrinks to the point *X* at the temperature 30.98°C. Above this temperature, no horizontal portion of the curve is pronounced and the isotherms approach more and more closely the ideal behaviour.

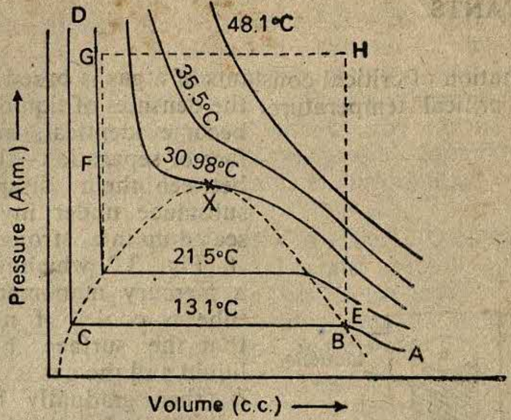


Fig. 3.1. Isotherms of CO_2.

It is evident from these considerations that within the dome-shaped area, obtained by joining the ends of the horizontal portions of the isotherms and the point *X*, both liquid and gaseous carbon dioxide exist. In the area to the left, only liquid is present and in the area to the right, only gaseous carbon dioxide will exist.

At the point *X*, it is not possible to distinguish gas from liquid and CO_2 exists in a state called critical state. The point *X* is known as the *critical point* and the temperature, pressure and volume corresponding to this point are called the critical temperature (T_c), critical pressure (P_c) and critical volume (V_c). For CO_2, T_c= 30.98°C, P_c=73 atm and V_c=94.9 cm^3/mole.

Similar isotherms are obtained for other gases. They will have characteristic T_c and P_c.

3.2. EXPERIMENTAL DETERMINATION OF CRITICAL CONSTANTS

The determination of critical constants of a gas is based on the fact that at the critical temperature, the densities of liquid and vapor become identical, and the surface of separation—the meniscus-between them disappears. The substance under investigation is sealed up in a strong glass tube *A*, Fig. 3.2, which is attached to a mercury manometer *B*. The tube is cooled if necessary, so that the surface between the liquid and the gas is apparent. It is then gradually heated in a suitable bath until the boundary between gas and liquid just disappears; this gives the critical temperature, and, the critical pressure can be obtained from the mercury level in the manometer. The critical volume can be obtained from the rule of Cailletet and Mathias.

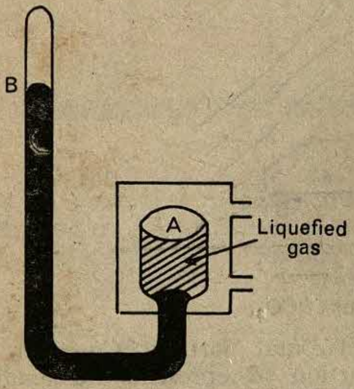


Fig. 3.2. Determination of critical constants.

This rule states that *when the mean values of the sum of the densities of liquid and saturated vapor of any substance are plotted against the temperature, the plot is a straight line, as shown in Fig. 3.3.* The densities of the liquid (d_l) and of the saturated vapor (d_v) in equilibrium with it are known as orthobaric densities. According to the law of Cailletet and Mathias, the equation of the line is

$$t=A+B\left(\frac{d_l+d_v}{2}\right) \quad \ldots (3.1)$$

where A and B are constants evaluated from the plot, and t is the temperature. At the critical temperature, $d_l=d_v=d_c$, where, d_c is the critical density. With this substitution equation (3.1) modifies to $t_c=A+Bd_c$ . . . (3.2)

Knowing the value of the critical temperature t_c, d_c, the critical density, can thus be obtained. From the critical density, the critical volume can be readily obtained.

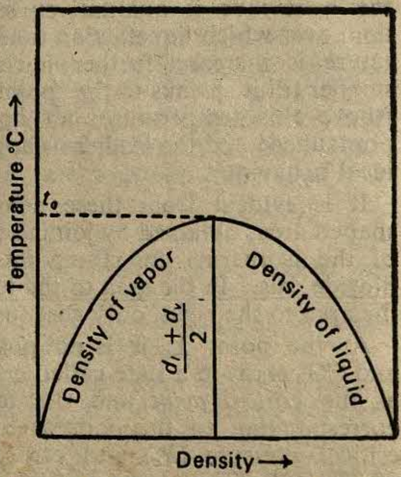


Fig. 3.3. Linear variation of mean density of a substance with temperature.

3.3. CONTINUITY OF STATE

In the preceding paragraph, it was said that within the dome, both gas and liquid exist in equilibrium while outside the dome either liquid or gas exists. Actually there is no dividing line between the liquid state and the gaseous state and there is a gradual transition from gas to liquid and vice-versa without any abrupt change in state. The fact that it is not always possible to make distinction between a gas and a liquid is known as the *principle of continuity of state.*

Consider again Fig. 3.1. Points E and F lie on the same isotherm (21.5°C). At point E, only gas exists and point F represents only liquid, obtained by compressing the gas isothermally. This change from gas to liquid at constant temperature can also be made without any sharp discontinuity. This is done as follows:

Let us increase the pressure of the gas at constant volume from point E to point H by increasing the temperature. After arriving at point H, the volume is decreased at constant pressure along the line HG by decreasing the temperature. After reaching the point G, the volume is kept constant and the temperature is decreased. This will result in the decrease of pressure until point F is reached. We see that in this series of changes, gaseous CO_2 can be converted to liquid without any abrupt change in state. It is not always possible to distinguish a gas from a liquid and the conversion of gas to liquid or vice-versa is continuous. The states in the region of point F can be taken as liquid states or highly compressed gaseous states depending upon the convenience.

The distinction between gas and liquid is possible only within the dome area where both are present in equilibrium and there is boundary surface. In the absence of this boundary surface, no fundamental distinction between gas and liquid is possible.

3.4. van der Waals EQUATION AND THE CRITICAL PHENOMENA

The van der Waals equation for one mole of gas is

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT \qquad \ldots (3.3)$$

On expanding and rearranging this equation in descending powers of V, we get

$$PV^3-V^2(RT+Pb)+aV-ab=0.$$

Division of the whole equation by P gives

$$V^3-V^2\left(b+\frac{RT}{P}\right)+V\left(\frac{a}{P}\right)-\frac{ab}{P}=0 \qquad \ldots (3.4)$$

This is a cubic equation in V which when solved for given values of P and T will yield either three values of V or one real and the other two imaginary. On substituting the experimental values of the constants a and b in equation (3.4), values of V for different values of P at known temperature are calculated. These values of V when plotted against P for a constant T give the various isotherms as shown in Fig. 3.4.

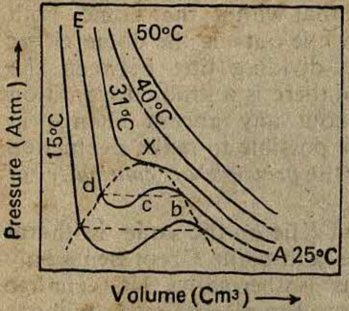


Fig. 3.4. Isotherms of CO_2 according to van der Waals equation.

It can be seen from the diagram that isotherms at 31°C (T_c) and above are exactly of the same type as shown in Fig. 3.1 but below 31°C, they differ. In each isotherm below the critical isotherm, the horizontal portion is omitted and replaced by a wave like portion (S-shaped). Consider, for example, the isotherm at 25°C. It is represented by *AbcdE*. As predicted by the van der Waals equation, it gives three values of V corresponding to the points b, c and d for the same value of pressure.

As the temperature rises, the wave like portion becomes smaller and smaller and the three possible values of V for a given P become closer and closer. At the critical temperature, the three values of V are identical. Above the critical temperature, each isotherm gives one real and two imaginary values for V for a given P.

It has been found that the portions *bc* and *cd* of the curve *AbcdE* can be realised under unstable conditions.

At the critical point X, the three values of V are not only real and positive but also identical and equal to the critical volume. Mathematically we have,

$$(V-V_c)^3=0 \qquad \ldots (3.5)$$

Expanding this equation by the binomial theorem we get:

$$V^3-(3V_c)V^2+(3V_c^2)V-V_c^3=0 \qquad \ldots (3.6)$$

Substituting P_c and T_c for P and T respectively in equation (3.4), we get:

$$V^3-V^2\left(b+\frac{RT_c}{P_c}\right)+V\left(\frac{a}{P_c}\right)-\frac{ab}{P_c}=0 \qquad \ldots (3.7)$$

On the basis of arguments given earlier, equation (3.7) should be identical with equation (3.6) and the coefficients of like term must be equal. Equating the coefficients of like powers of V in equations (3.6) and (3.7), we get

$$3V_c=b+\frac{RT_c}{P_c} \qquad \ldots (3.8)$$

$$3V_c^2=\frac{a}{P_c} \qquad \ldots (3.9)$$

and

$$V_c^3=\frac{ab}{P_c} \qquad \ldots (3.10)$$

Dividing the equation (3.10) by equation (3.9),

$$V_c=3b$$

Substituting this value of V_c in equation (3.9) ... (3.11)

$$3(9b^2)=\frac{a}{P_c} \quad \text{or} \quad P_c=\frac{a}{27b^2} \qquad \ldots (3.12)$$

Substituting the values of V_c and P_c from equations (3.11) and (3.12) respectively, in equation (3.8);

$$3\times 3b=b+\frac{RT_c}{b}\times 27b^2$$

or

$$T_c=\frac{8a}{27Rb} \qquad \ldots (3.13)$$

From equation (3.12),

$$a=P_c\times 27b^2$$

Substituting this value in equation (3.13),

$$T_c=\frac{8\times P_c\times 27b^2}{27Rb}$$

or

$$b=\frac{RT_c}{8P_c} \qquad \ldots (3.14)$$

Substituting this value of b in equation (3.13) yields

$$T_c=\frac{8a\times 8P_c}{27R\times RT_c}$$

or

$$a=\frac{27R^2T_c^2}{64P_c} \qquad \ldots (3.15)$$

With the help of equations (3.14) and (3.15), values of the critical constants can be easily calculated from a knowledge of P_c and T_c and using the corresponding values of R. The results when compared with the experimental values of a and b showed that the two values agree near the critical point but disagree when moved away from critical point.

On eliminating b from equation (3.8),

$$3V_c=\frac{V_c}{3}+\frac{RT}{P_c}$$

or

$$\frac{RT_c}{P_cV_c}=\frac{8}{3}=2.67 \qquad \ldots (3.16)$$

Equation (3.16) shows that if the van der Waals equation is valid near the critical point, the values of $\frac{RT_c}{P_cV_c}$ calculated for various gases should be 2.67 but it is found that the values are generally higher than 2.67 and are different for different gases. This is due to the fact that the correction term $\frac{a}{V^2}$ for the molecular forces in the van der Waals equation does not give the true intermolecular attraction when the molecules are very close to one another as near the critical point.

Problem 3.1. Calculate V_c, P_c and T_c for carbon dioxide gas. The values for the van der Waals constants for CO_2 are

$$a=3.60 \text{ litre}^2 \text{ atm mole}^{-2} \text{ and } b=4.28\times10^{-2} \text{ litre mole}^{-1}$$

Solution.

$$V_c=3b$$
$$=3\times4.28\times10^{-2} \text{ litre mole}^{-1}$$
$$=1.28\times10^{-2} \text{ litre mole}^{-1}$$

$$P_c=\frac{a}{3V_c^2}$$
$$=\frac{3.60 \text{ litre}^2 \text{ atm mole}^{-2}}{3\times(1.28\times10^{-1} \text{ litre mole}^{-1})^2}$$
$$=7.32 \text{ atm}$$

and

$$T_c=\frac{8a}{27Rb}$$
$$=\frac{8(3.60) \text{ litre}^2 \text{ atm mole}^{-2}}{27(0.082 \text{ litre atm deg}^{-1} \text{ mole}^{-1})(4.28\times10^{-2} \text{ litre mole}^{-1})}$$
$$=304\text{K}$$

3.5. THE LAW OF CORRESPONDING STATES

van der Waals in 1881 showed that if the pressure, volume and temperature of a gas are expressed as fractions of critical pressure, critical volume and critical temperature in his equation, an important generalization known as the law of corresponding states is obtained.

Let $\pi=\frac{P}{P_c}$ or $P=\pi P_c$

$\phi=\frac{V}{V_c}$ or $V=\phi V_c$

and $\theta=\frac{T}{T_c}$ or $T=\theta T_c$

π, ϕ and θ are called the reduced pressure, the reduced volume and the reduced temperature respectively.

Substituting these values of P, V and T in the van der Waals equation, we get

$$\left(\pi P_c+\frac{a}{\phi^2 V_c^2}\right)(\phi V_c-b)=R\theta T_c \qquad \ldots (3.17)$$

Since $P_c=\frac{a}{27b^2}$, $V_c=3b$ and $T_c=\frac{8a}{27Rb}$, equation (3.17) takes the form

$$\left(\pi \cdot \frac{a}{27b^2}+\frac{a}{9\phi^2\,b^2}\right)(3\phi b-b)=R\theta\,\frac{8a}{27Rb}$$

or
$$\frac{a}{27b^2}\left(\pi+\frac{3}{\phi^2}\right)b(3\phi-1)=\frac{a}{27b}\cdot 8\theta$$

or
$$\left(\pi+\frac{3}{\phi^2}\right)(3\phi-1)=8\theta \qquad \ldots (3.18)$$

Equation (3.18) is known as the *van der Waals reduced equation of state.* This equation does not involve either R or the van der Waals constants a and b which are characteristic of the given gas. Hence it is a perfectly general equation and is applicable to all liquids and gases.

It is evident from equation (3.18) that when two or more substances have the same reduced temperature and reduced pressure, they will have the same reduced volume. Thus two or more substances under these conditions are said to be in corresponding states and the above statement is referred to as the law of corresponding states.

The law of corresponding states is not rigorously valid but is only approximately true. This can easily be shown by drawing the graphs in terms of the reduced pressure and reduced volume for different substances at the same reduced temperature. The curves are found not coinciding with each other.

Problem 3.2. Calculate the value of the pressure for 1 mole of CO_2 at 40°C when confined in a volume of 0.107 litre using (*a*) the law of corresponding states, and (*b*) the ideal gas law. Given that P_c for CO_2 is 73 atm at 40°C.

Solution. (*a*) The reduced pressure π is given by the relation.

$$\pi=\frac{8\phi}{3\phi-1}-\frac{3}{\phi^2}$$

where
$$\pi=\frac{P}{P_c},\ \theta=\frac{T}{T_c} \text{ and } \phi=\frac{V}{V_c}$$

$$=\frac{8T/T_c}{(3V/V_c)-1}-\frac{2}{(V/V_c)}$$

$$=\frac{8}{3(0.107)/(0.0957)-1}\times\frac{313.2}{304.2}-\frac{3}{(0.107/0.0957\text{ litre})^2}$$

$$=\frac{8}{3\times1.118-1}\times1.03-\frac{3}{(1.1)^2}$$

$$=\frac{8}{2.35}\times1.03-\frac{3}{1.21}$$

$$=3.51-2.40=1.11$$

Thus,
$$P=\pi P_c=73.0\times1.11=81 \text{ atm.} \quad \textbf{Ans.}$$

(*b*)
$$P=\frac{RT}{V}$$

$$=\frac{0.0821\text{ litre atm deg}^{-1}\text{ mole}^{-1}\times313.2}{0.107\text{ litre mole}^{-1}}$$

$$=240 \text{ atm.} \quad \textbf{Ans.}$$

3.6. LIQUEFACTION OF GASES

A gas can be liquefied by applying high pressure and decreasing the temperature. Compression of the gas brings the molecules closer and a decrease in temperature reduces the kinetic energy of the molecules.

Faraday (1823) was the first to try joint application of cooling and compression for the liquefaction of various gases. He employed a V shaped tube, in one limb of which the gas was prepared and in the other limb, which was immersed in an ice chamber, the gas was liquefied under its own pressure. By applying this method, Faraday could liquefy many of the gases *e.g.*, Cl_2, SO_2, H_2S, CO_2, HCl, NH_3 etc. but failed to liquefy gases such as O_2, N_2 and H_2 though he applied very high pressure (upto 3000 atm). He referred to these gases as permanent gases.

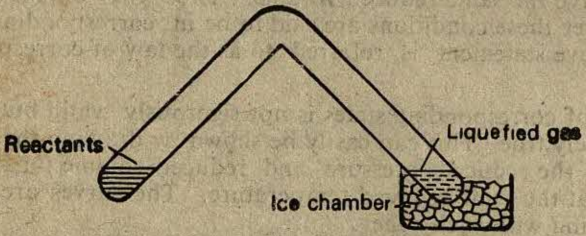


Fig. 3.5. Faraday's apparatus for the liquefaction of gases.

The reason for the failure in the liquefaction of the so-called permanent gases was given by Andrews in 1863 when he investigated the critical phenomena. He said that a gas must be cooled below its critical temperature before it can be liquefied. If the gas is above its critical temperature, it cannot be liquefied however high pressure may be applied. Since the critical temperature of the permanent gases was found to be very low, therefore, Faraday failed to liquefy them. Thus it is clear that the liquefaction of the permanent gases requires intense cooling and considerable high pressure.

Pictet (1877) for the first time succeeded in liquefying oxygen and hydrogen and showed that these are no longer permanent gases. He employed the *Principle of Cascades* or *Series Refrigeration* by which gases having sufficiently low critical temperature are cooled by evaporating a liquefied gas. For example, by evaporating the liquid sulphur dioxide, a temperature of —65°C was obtained which was sufficient to liquefy carbon dioxide. Similarly, vaporisation of the liquid carbon dioxide brought down the temperature to —130°C which was sufficient to liquefy the compressed oxygen. Using the cascade method, the lowest temperature that could be achieved by evaporation of liquid oxygen was —218°C which was much higher than the critical temperature of neon ($T_c = -228.71$°C), hydrogen ($T_c = -239.91$°C) and helium ($T_c = -267.84$°C).

To attain these low temperatures, the following two methods are most widely employed:

(1) *The Linde's and Hampson's* (*1895*) *method employing the Joule-Thomson effect to cause cooling*; and

(2) *The Claude's and Heylan's method which is based on cooling due to adiabatic expansion.*

The Linde's and Hampson's method. Their method is based on the Joule-Thomson effect according to which when a gas under high pressure is allowed to expand into a region of low pressure, it falls in temperature. The gas is cooled due to the fact that during expansion, the internal energy is used to overcome the attractive forces between the molecules. The apparatus used by Linde for the liquefaction of air is shown in Fig. 3.6.

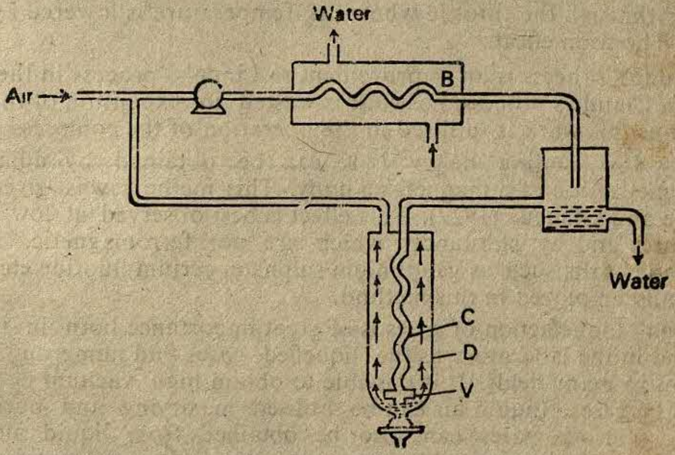


Fig. 3.6. Linde's apparatus for the liquefaction.

The air to be liquefied is first purified and then compressed to a pressure of about 200 atm. by the compressor. During compression, heat is generated which is removed by passing the gas through water cooled copper coils, *B*. Also during compression, if there is any water in the air, it condenses and is removed as shown in the diagram. The air thus dried is passed through copper tubes coiled in the form of spirals *C* and is allowed to expand suddenly in the chamber *D* to a pressure of about one atmosphere by regulating the valve *V*. Due to expansion, the temperature of the air falls to about −78°C. The air thus cooled again passes over the copper spirals *C* and in this way cools the incoming air even more before expansion. After the completion of the cycle several times, the temperature of the expanding gas becomes so small that liquid air begins to issue through the valve *V*. The air which is not condensed goes back to the compressor and the whole cycle is completed.

It was observed that while most of the gases were cooled during expansion, hydrogen and helium warmed up. On investigation it was found that both hydrogen and helium behaved in the same manner as other gases if before expansion, they were cooled below their inversion temperature. For H_2 and He, the inversion temperature is —80°C and —240°C respectively.

The Claude's Method. In this method, the gas is cooled due to the work done by the gas in its adiabatic expansion. The gas is compressed to about 200 atmospheres and is then allowed to expand against a confining piston. During expansion against the piston, the gas has to do some mechanical work. As a result of this work, the kinetic energy of the gas molecules is removed and the temperature falls. The issuing gas is divided into two streams—one is again allowed to do work in expansion against the piston and the other is passed through the throttle where its temperature is lowered by the Joule-Thomson effect.

Claude's process is an improvement to Linde's process in the fact that in Claude's process, no work is wasted in expansion of the gas and thus this work is utilised in the operation of the compressors.

Very low cooling below 1 K can be obtained by adiabatic demagnetisation of a magnetised body. This method was given by Debye and Giaqeue (1927). This effect is best observed at low temperatures and by substances which are not ferromagnetic. Paramagnetic salts such as gadolinium sulphate, cerium fluoride etc., are generally employed in this method.

Uses. Liquefaction of gases is of great importance both in industry and in the laboratory as the liquefied gases find numerous applications in many fields. It is possible to obtain high vacuum by using liquefied gases. Liquid air can be utilised in drying and purifying gases. Various gases can also be obtained from liquid air *e.g.*, oxygen, argon, neon and krypton are obtained on a large scale by the fractional distillation of the liquid air. Gases which can be easily liquefied *e.g.*, sulphur dioxide, ammonia, difluoro—dichloromethane (freon) etc.. can be used for refrigeration purposes. Liquid oxygen, when mixed with powdered charcoal and detonated, can be employed for preparing explosives. These days oxygen and helium are being used for welding purposes on a large scale. Liquid chlorine has outdated bleaching powder and is now most commonly employed for bleaching purposes.

3.7. STRUCTURE OF LIQUIDS

A liquid may be regarded as a continuation of a gas phase into the region of small volumes and very high molecular attractions. Our present knowledge about the nature of the liquid state is still very incomplete. There are two main theories of liquid structure.

One theory considers liquid as an imperfect gas. This is supported by the fact that above the critical point there is no distinction at all between the liquid and a gas and the so-called fluid state of matter exists.

The second view point about the structure of liquid considers it similar to a crystal, except that the well ordered arrangement of the liquid extends over to only five or six molecular diameters. This is often referred to as short-range order and long-range disorder. It is more plausible model since near the melting point, the densities of crystal and liquid lie close together. Whatever order exists in a liquid structure, it is continuously changing because of the thermal motions of the individual molecules. The properties of liquids are determined by a time average of a large number of different arrangements.

A more direct approach to liquids is provided directly from the fundamentals of inter-molecular forces and statistical mechanics.

PROBLEMS

1. Give an account of Andrews experiment on critical phenomenon with CO_2 and the important conclusion that can be drawn from it.

2. Show that for one mole of a real gas, $V_c=3b$, $P_c=\frac{a}{27b^2}$, $T_c=\frac{8a}{27Rb}$ where V_c is the critical volume, P_c is the critical pressure and T_c is the critical temperature.

3. What do you understand by "continuity of state?" Explain with the help of isotherms of carbon dioxide.

4. The Berthelot equation of state (for one mole of gas) $P+\frac{a}{TV_2}(V-b)=RT$ is more useful than the van der Waals equation at pressures below 1 atm., (*i*) Evaluate a, b and R in terms of the critical constants. (*ii*) Derive the reduced equation of state.

Ans. (*i*) $a=3P_cV_c^2$, $b=1/3\ V_c$, $R=8/3\ \frac{P_cV_c}{T_c}$

(*ii*) $(\pi+3)(3\theta-1)=8\ \theta$.

5. Calculate the constants 'a' and 'b' for a gas obeying van der Waals equation of state if the critical temperature and critical pressure of the gas are 31°C and 72.8 atm. respectively. The value of $R=0.08206$ litre atmospheres deg^{-1} $mole^{-1}$.

Ans. $a=3.606$ litre^2—atm. mole^{-2}.

$b=42.83$ cc. mole^{-1}.

6. Calculate the values of critical temperature and critical pressure of CO_2. The van der Waal constant a and b for CO_2 are 1.362 litre^2 atm mole^{-2} and 3.19×10^{-2} litre mole^{-1} respectively. The value of $R=0.082$ litre-atmospheres deg^{-1} mole^{-1}.

Ans. $T_c=$—118.7, $P_c=49.7$ atm.

7. Prove that for a gas obeying van der Waals equation, $\frac{RT_c}{P_cV_c}=\frac{8}{3}$ where R

is the gas constant and T_c, P_c and V_c are the critical temperature, critical pressure and critical volume of gas respectively. How far does a real gas obey van der Waals equation?

8. Discuss the various methods that have been adopted for the production of cold. What is the lowest temperature so far reached? How has it been reached?

9. Write short notes on the following:
   - (*a*) Law of corresponding states.
   - (*b*) Structure of Liquids.

Chapter 4

PROPERTIES OF LIQUIDS

4.1. VAPOR PRESSURE

A liquid when placed in a container will partially evaporate and the molecules of the vapor would exert a definite pressure on the liquid. Consider, for example, liquid bromine sealed up in an evacuated vessel as shown in Fig. 4.1. It will be observed that some of the bromine molecules in the vapor state would escape in the space above it (indicated by the brown colour in the vapor state). Since the space is limited by the closed vessel, the molecules return to the liquid. This moving up of the molecules is called *vaporisation* or *evaporation* and returning of the vapors to the surface of the liquid is called *condensation*. When the process of evaporation and condensation are in equilibrium with each other, pressure exerted would then be the saturated *vapor pressure* or *vapor pressure* of the liquid.

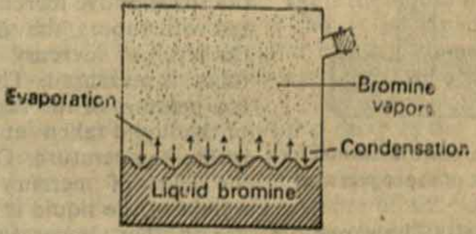


Fig. 4.1. Vapor pressure of liquids.

The phenomena of vapor pressure can be readily explained from the Kinetic Theory of the gases. Molecules in a liquid, like gas molecules, are in a state of motion moving with different velocities. Some of the molecules moving in the direction of the surface and possessing sufficient kinetic energy to overcome the forces of attraction of other molecules in the liquid state would leave the surface of liquid, accumulate in the space above the liquid and exert a vapor pressure. However, some molecules in the space strike the surface and will be retained by the liquid. At equilibrium, the rate of escape of molecules from the surface is equal to the rate of return of molecules to the surface and the pressure exerted will then be the vapor pressure of liquid.

Vaporisation of a liquid is an endothermic process, as it is accompanied by the absorption of heat. Heat supplied increases the kinetic energy of the molecules in the liquid. When kinetic energy of the molecules in the liquids becomes sufficiently high to overcome cohesive forces, evaporation sets in. For any definite quantity of liquid at a definite temperature, the amount of heat required to vaporise it is known as the (latent) heat of vaporisation of the liquid. If the quantity of the liquid is one mole, the expression *molar heat of vaporisation* is used which means the amount of heat required to convert one mole of liquid into the vapor state.

Determination of vapor pressure. The various methods frequently employed for measuring the vapor pressure of a liquid may be classified into three categories: (*i*) Static Methods; (*ii*) Dynamic Methods; and (*iii*) Gas Saturation Methods.

Static Methods. The two methods used here are given below:

(*a*) *The Barometric method.* This is the simplest method. This involves two barometer tubes which are filled with mercury and inverted over mercury as shown in Fig. 4.2. One of the tubes is used for comparison purposes. The liquid whose vapor pressure is to be determined is passed up into the other tube by means of a bent pipette. After some time, when the space above mercury is saturated with vapors, the difference in the levels of mercury in the two tubes is measured. This difference is a measure of the vapor pressure of the liquid taken at the experimental temperature. Depression in the level of mercury due to the weight of the liquid is taken to be negligibly small. The vapor pressure at other temperatures can also be measured with this apparatus by surrounding the barometer tubes with a heating jacket.

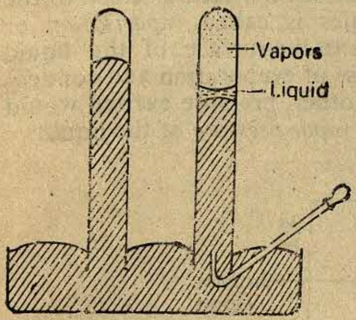


Fig. 4.2. The Barometric method for the measurement of vapor pressure.

(*b*) *Isoteniscope method.* This method is given by Smith and Menzies (1910). The instrument, which they used, is known as the Isoteniscope and is shown in Fig. 4.3.

The liquid whose vapor pressure is to be determined is filled up about one half in the isoteniscope bulb *B*. This bulb is attached to a U-tube which contains the same liquid. The level of the liquid is about half way up the limbs of U tube. This set is called as the isoteniscope. This is then attached to a manometer and a large regulator bottle *C*. Pressure fluctuations can be minimised with the help of this regulator bottle. The isoteniscope is maintained at a constant temperature by immersing it in a water bath *D*, the temperature of which is determined by immersing a thermometer in it.

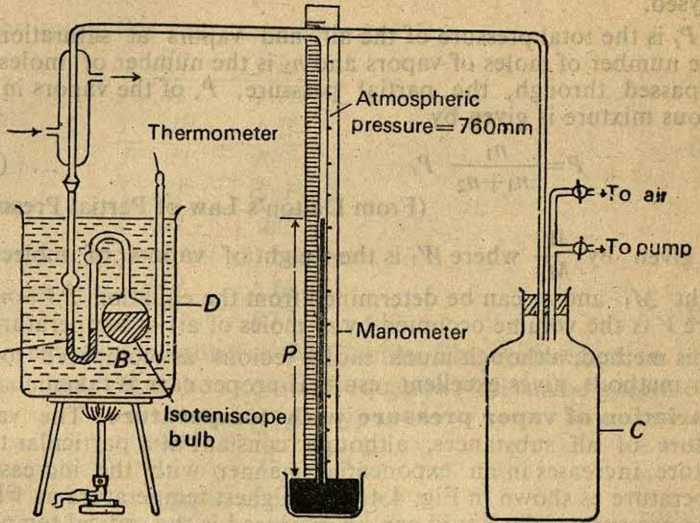


Fig. 4.3. The isoteniscope method for the measurement of vapor pressure.

To start with, the apparatus is first evacuated by connecting the regulator bottle to a suction pump until the liquid in the bulb *B* begins to boil and the whole air from *B* and *A* is expelled. Suction pump is then turned off and the regulator bottle is connected to air so that air is admitted to the system until the level of the liquid is exactly equal in the limbs of U-tube. Under these conditions, the pressure above the liquid in the tube is the same as the pressure in the regulator bottle and is given by the difference between the barometric pressure and the height of mercury colomn in the manometer. In the same manner, the vapor pressure of the liquid can be recorded at different temperatures by simply changing the temperature of the water bath.

This method is very convenient and gives results with a fair degree of accuracy.

The dynamic method. In this method, the liquid is boiled under a fixed external pressure. The temperature at which the liquid boils is noted by a thermometer which is placed in the condensing vapor to avoid error due to superheating of the liquid. Since boiling point of a liquid is defined as the temperature at which vapor pressure of the liquid is equal to the external pressure; the reading, therefore, gives the vapor pressure equal to the external pressure.

The gas saturation method. This method involves the saturation of dry air or some inert gas with the vapors of the liquid by bubbling a known quantity of the gas through the liquid at constant temperature. The gas saturated with the vapors of the liquid is then either considered or absorbed by suitable absorbing agents and analysed.

If P_t is the total pressure of the air and vapors at saturation, n_1 is the number of moles of vapors and n_2 is the number of moles of gas passed through, the partial pressure, P, of the vapors in the gaseous mixture is given by

$$P=\frac{n_1}{n_1+n_2}P_t \qquad \ldots (4.1)$$

(From Dalton's Law of Partial Pressure)

n_1 is given by $\frac{W_1}{M_1}$ where W_1 is the weight of vapors of molecular weight M_1 and n_2 can be determined from the equation $P_tV=n_2RT$ where V is the volume occupied by n_2 moles of air at temperature T.

This method, although much more tedious as compared to the other methods, gives excellent results if proper care is taken.

Variation of vapor pressure with temperature. The vapor pressure of all substances, although constant at a particular temperature, increases in an exponential manner with the increase of temperature as shown in Fig. 4.4. The highest temperature at which vapor pressure of the liquid can be measured is the critical temperature and the lowest temperature at which vapor pressure of the liquid can be measured in the freezing point. Above critical temperature and below freezing point, liquid does not exist.

The variation of vapor pressure with temperature can be expressed mathematically with the help of an equation derived thermodynamically by Clapeyron and later developed by Clausis. The Clapeyron equation for the vaporisation of a liquid can be written as:

$$\frac{dP}{dT}=\frac{\triangle H_v}{T(V_v-V_l)} \qquad \ldots (4.2)$$

$\frac{dP}{dT}$ represents the change in vapor pressure of the liquid with change in temperature. $\triangle H_v$ is the heat of vaporisation per mole of the liquid, V_v the molar volume of the vapors and V_l is the molar volume of the liquid—all at the same absolute temperature T.

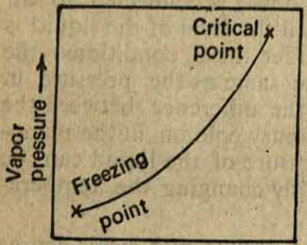


Fig. 4.4. Variation of vapor pressure with temperature.

If the temperature is quite far off from the critical temperature, V_l will be negligibly small as compared to V_v and equation (4.2) becomes

$$\frac{dP}{dT}=\frac{\triangle H_v}{TV_v} \qquad \ldots (4.3)$$

If it is assumed that vapors behave just like an ideal gas,

$$V_v = \frac{RT}{P} \qquad \ldots (4.4)$$

Substituting this value in equation (4.3)

$$\frac{dP}{dT} = \frac{\triangle H_v . P}{T . RT}$$

or

$$\frac{1}{P}\frac{dP}{dT} = \frac{\triangle H_v}{RT^2} \qquad \ldots (4.5)$$

Since

$$\frac{1}{P}\frac{dP}{dT} = \frac{d\ln P}{dT}$$

Therefore, equation (4.5) becomes

$$\frac{d\ln P}{dT} = \frac{\triangle H_v}{RT^2} \qquad \ldots (4.6)$$

This equation is known as the Clausius-Clapeyron equation.

Assuming $\triangle H_v$ to be a constant, equation (4.6) can be integrated as

$$\int d\ln P = \frac{\triangle H_v}{R}\int \frac{dT}{T^2} \qquad \ldots (4.7)$$

$$\ln P = -\frac{\triangle H_v}{RT} + C' \qquad \ldots (4.8)$$

where C' is a constant of integration. Converting the natural logarithm to the base 10,

or

$$\log_{10} P = -\frac{\triangle H_v}{2.303R}\left(\frac{1}{T}\right) + C \qquad \ldots (4.9)$$

where C is another constant.

Equation (4.9) is similar to the equation for a straight line. Hence plot between $\log_{10} P$ and $\frac{1}{T}$ should be a straight line with the slope equal to $\frac{-\triangle H_v}{2.303R}$ and intercept on the y-axis equal to C. Such a plot for various liquids is shown in Fig. 4.5. The results are in agreement with equation (4.9).

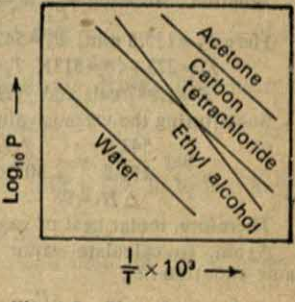


Fig. 4.5. Plot of $\log_{10} P$ vs $1/T \times 10^3$ for various liquids.

Equation (4.9) can also be written in a more convenient form. This is done by integrating equation (4.6) between the limits P_1 and P_2 which are the vapor pressures corresponding to the temperatures T_1 and T_2 as given below:

$$\int_{P_1}^{P_2} d\ln P = \frac{\triangle H_v}{R}\int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\ln \frac{P_2}{P_1} = \frac{\triangle H_v}{R}\left[-\frac{1}{T}\right]_{T_1}^{T_2}$$

$$= \frac{\triangle H_v}{R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

or $$\log_{10} \frac{P_2}{P_1} = \frac{\triangle H_v}{2.303R}\left[\frac{T_2 - T_1}{T_2 T_1}\right] \qquad \ldots (4.10)$$

Equation (4.10) permits the calculation of $\triangle H_v$ if the values of vapor pressure, P_1 and P_2, are known at the temperatures, T_1 and T_2 respectively. Alternatively, if $\triangle H_v$ is given, pressure at any desired temperature can be calculated by knowing the vapor pressure at other temperature.

Problem 4.1. The vapor pressure of methyl chloride between —47°C and —10°C can be represented by an equation

$$\log p_{mm} = \frac{-1149}{T} + 7.481$$

What is the heat of vaporisation of the liquid in calories/gram?

Solution. Since $\triangle H_v = -2.303 \times 1.987 \times \text{slope}$

Again in the equation

$$\log p_{mm} = \frac{-1149}{T} \times 7.481, \text{ slope} = -1149$$

Therefore, $\triangle H_v = -2.303 \times 1.789 \times (-1149)$
$= 5258$ cals/mole.

Now, molecular weight of methyl chloride = 50.5.

Therefore, heat of vaporisation per gram of the liquid

$$= \frac{5258}{50.5} = 104.1 \text{ cals.}$$

Problem 4.2. The vapor pressure of ethanol is 135.5 mm at 40°C and 542.5 mm at 70°C. Calculate the molar heat of vaporisation and also vapor pressure of ethanol at 50°C.

Solution. Since $\log \frac{P_2}{P_1} = \frac{\triangle H_v}{2.303R}\left(\frac{T_2 - T_1}{T_2 T_1}\right)$

Here $P_1 = 135.5$ mm, $P_2 = 542.5$

$T_1 = 273 + 40 = 313\text{K}$ $T_2 = 273 + 70 = 343\text{K}$

$R = 1.987$ cals and $\triangle H_v = ?$

Substituting the various values,

$$\log \frac{542.5}{135.5} = \frac{\triangle H_v}{2.303 \times 1.987}\left(\frac{343 - 313}{343 \times 313}\right)$$

or $\triangle H_v = 98$

Therefore, molar heat of vaporisation of ethonal is 9877 cals.

Again, to calculate vapor pressure of ethanol at 50°C, we make use of the same equation *i.e.*,

$$\log \frac{P_2}{P_1} = \frac{\triangle H_v}{2.303R}\left(\frac{T_2 - T_1}{T_2 T_1}\right)$$

Here $\triangle H_v = 9877$

$P_2 = 542.5$ mm $\quad P_1 = ?$

$T_2 = 343\text{K} \quad T_1 = 273 + 50 = 323\text{K}$

and $R = 1.987$ cals.

Substituting these values

$$\log \frac{542.5}{P_1} = \frac{9877}{2.303 \times 1.987}\left(\frac{343 - 323}{343 \times 323}\right)$$

or $$P_1 = 221.2 \text{ mm.}$$

Therefore, vapor pressure of ethanol at 50°C = 221.2 mm.

4.2. BOILING POINT

The boiling point of a liquid is defined as the temperature at which vapor pressure of the liquid becomes equal to the external pressure. Consider, for example, water as the liquid at an atmospheric pressure of 760 mm Hg or 1 atmosphere. On heating the water, its vapor pressure gradually increases. At 100°C, the vapor pressure of water becomes 760 mm Hg. Hence, water will boil at a temperature of 100°C because at this temperature, its vapor pressure becomes equal to the external pressure. If the external pressure is 1 atmosphere, the term normal boiling point is used.

Boiling point relationships. The following are some important relationships with boiling point:

(*i*) The boiling point of a liquid T_b, at 1 atmospheric pressure, is about two-thirds of the critical temperature *i.e.*,

$$T_b = \tfrac{2}{3} T_c$$

or $$T_b = 0.667\, T_c \qquad \ldots (4.11)$$

Both the temperatures should be expressed in absolute degrees.

(*ii*) The ratio of molar heat of vaporisation in calories of a liquid to its normal boiling point on the absolute scale is constant *i.e.*,

$$\frac{\Delta H_v}{T_b} = \text{Constant}$$

The constant for most of the liquids is approximately equal to 21.

Therefore, $$\frac{\Delta H_v}{T_b} \approx 21 \text{ cals mole}^{-1} \text{ deg}^{-1} \qquad \ldots (4.12)$$

Equation (4.12) is known as the Trouton's Rule. The quantity $\frac{\Delta H_v}{T_b}$ is called as the 'entropy of vaporisation.'

Trouton's Rule is approximately correct and a few liquids obey it. It has no theoretical justification.

Problem 4.3. The normal boiling point of benzene is 353.3 K. Assuming the applicability of Trouton's Rule, estimate the boiling point of liquid under a reduced pressure of 25 mm.

Solution. According to Trouton's Rule,

$$\frac{\Delta H_v}{T_b} = 21$$

Here $T_b = 353.3$ K, $\Delta H_v = ?$

Therefore, $\Delta H_v = 353.3 \times 21 = 7419.3$ cal/mole.

In order to determine the boiling point of benzene under a reduced pressure of 25 mm

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R}\left(\frac{T_2-T_1}{T_2T_1}\right)$$

Here $P_2=760$ mm $P_1=25$ mm

$T_2=353.3$ K $T_1=?$

$\Delta H_v=7419.3$ cal/mole and $R=1.987$ cals.

Substituting these values,

$$\log \frac{760}{25} = \frac{7419.3}{2.303\times1.987}\left(\frac{353.3-T_1}{T_1\times353.3}\right)$$

or $T_1=267.1$ K

Therefore, boiling point of liquid under a reduced pressure of 25 mm $=267.1$ K.

4.3. SURFACE TENSION

Consider a molecule, *A*, in the interior of a liquid. It is being attracted by neighbouring molecules equally in all directions and thus the resultant force on it is zero. Now consider another molecule, *B* at the surface. It is experiencing a resultant force downward because of greater attraction for molecules in the liquid than for molecules in the vapor above the liquid. This is the case with all the molecules at the surface. As a result of this inward pull, all the molecules at the surface tend to go down and in doing so make the liquid behave as if it were enclosed by a membrane or skin. Thus the surface of the liquid tends to contract to have the minimum surface area possible. This force in the surface of a liquid is called *surface tension* and is defined as the *force in dynes acting at right angles upon a line of 1 cm length in the surface.* It is because of surface tension that falling water droplets in vacuum and the mercury particles on a smooth surface acquire spherical shape (*A* sphere occupies a smallest area for the given volume).

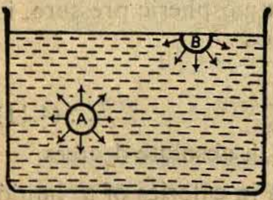


Fig. 4.6. Force acting on a molecule in a liquid.

Since every liquid has a tendency to decrease its surface area, therefore, it is necessary to do work against the inward pull and to bring molecules from the interior of the liquid in the surface in order to increase the surface area of the liquid. To obtain an expression for this work, consider a film of liquid stretched on a rectangular wire frame, one side of which is movable.

Let a force, *F* is applied perpendicular to the movable side to move it against the force of surface tension. If the wire moves a distance, *dx*, the work done, *W* is given by

$$W=Fdx \qquad \ldots (4.13)$$

This causes an increase in the surface area of the film given by

$$\triangle A=2(l\times dx) \qquad \ldots (4.14)$$

where l is length of the film. The factor 2 is introduced because there are two sides of the film.

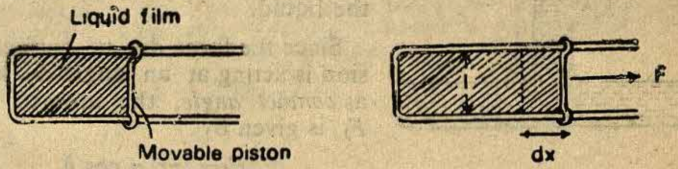


Fig. 4.7. Calculation of force on a liquid surface.

Since the force F is applied against the force of surface tension acting on the film, therefore, if γ is the force per centimetre along the movable wire, then

$$F=\gamma\times 21 \qquad \ldots (4.15)$$

$$\left(\gamma=\frac{F}{2l}=\frac{\text{Force}}{\text{Unit length}}\right)$$

Therefore, $W=\gamma.2ldx$

$=\gamma.\triangle A$ (vide equation 4.14)

or $$\gamma=\frac{W}{\triangle A}=\frac{\text{Work}}{\text{Area}} \qquad \ldots (4.16)$$

From equation (4.15), surface tension is defined as the force in dynes acting per unit length and from equation (4.16), it can be defined as the work in ergs required to generate a unit increase in surface area. The units of surface tension are dynes/cm or ergs/cm^2. SI units of surface tension is newton/m.

Measurement of Surface Tension

The various methods which are commonly employed to determine the surface tension of a liquid are:

(*i*) **The capillary rise method**. This method is based on the fact that any liquid such as water which wets the walls of a glass capillary tube will rise in the tube when the tube is placed in the liquid. On the other hand, if a liquid such as mercury which does not wet the walls of the capillary tube will not rise and show a depression in the level of the liquid in the capillary tube. The rise or fall of a liquid in a capillary tube is based on the surface tension.

Consider a fine capillary tube of uniform radius, r, placed in a liquid that wets the walls of the tube. Because of force of surface tension, γ, which acts along the inner circumference of the liquid, liquid will rise. The liquid keeps on rising until upward force, F_1, due to surface tension is balanced by the downward force, F_2, due to the weight of the liquid.

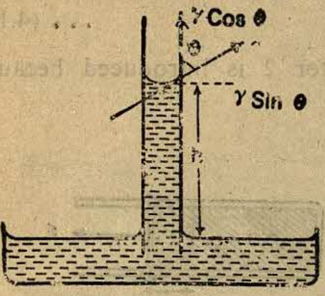


Fig. 4.8. Capillary rise method for measuring surface tension.

Since the force due to surface tension is acting at an angle θ, known as *contact angle*, the upward force. F_1, is given by

$$F_1 = 2\pi r.\,\gamma\cos\theta \quad \ldots (4.17)$$

If the liquid rises a height h in the tube above the level of the liquid outside, the downward force, F_2, is given by

$$F_2 = \pi r^2.h\,dg \quad \ldots (4.18)$$

where d is the density of the liquid and g is the gravitational force. At equilibrium, the two forces are equal.

Therefore, $F_1 = F_2$

From equations (4.17) and (4.18)

$$2\pi r.\gamma\cos\theta = \pi r^2.h\,dg$$

or

$$\gamma = \frac{1}{2\cos\theta}.\,r\,h\,dg \quad \ldots (4.19)$$

For many liquids, θ is approximately zero.

Therefore, $\cos\theta = 1$

and

$$\gamma = \tfrac{1}{2}\,r\,h\,dg \quad \ldots (4.20)$$

From this equation, surface tension of a liquid of known density can be calculated by determining the height to which it rises in the tube of known radius.

For accurate works, the following two corrections should be made:

(*i*) Correction for the volume of the meniscus.

(*ii*) Correction for the density of the vapors collected above the liquid. Considering these corrections, equation (4.20) is modified as

$$\gamma = \tfrac{1}{2}\left(h + \frac{r}{3}\right)(d_l - d_v)rg \quad \ldots (4.21)$$

where d_l is the density of the liquid and d_v is the density of the vapor above the liquid.

This is the most accurate method for determining surface tension of a liquid.

Problem 4.4. The radius of a given capillary is 0.0335 cm. A liquid whose density is 0.866 grams/cm^3 rises to a height of 2.0 cm in the capillary when it is dipped in the liquid. Calculate the surface tension of the liquid.

Solution. Since $\gamma = \frac{1}{2} r h d g$

Here $r = 0.0335$ cm, $h = 2.0$ cm.

$d = 0.866$ gram/cm^3 and $g = 981$

Therefore, $\gamma = \frac{1}{2} \times 0.0335 \times 2.0 \times 0.866 \times 981$

$= 28.46$

Thus, surface tension of the liquid = 28.46 dynes/cm.

Problem 4.5. At 20°C, the surface tension of chloroform is 16.2 dynes/cm. The densities of liquid and gas at the same temperature are 0.9188 gm/cm^3 and 0.0110 gram/cm^3. If the radius of capillary is 0.105 mm, what would be the height of the liquid in the capillary, angle of contact being zero?

Solution. $\gamma = \frac{1}{2}\left(h + \frac{r}{3}\right)(d_l - d_v)\, g r.$

Here $\gamma = 16.2.$ $h = ?$

$d_l = 0.9188,$ $d_v = 0.0110,$

$g = 981$

and $r = 0.0105$ cm.

Substituting these values,

$$16.2 = \frac{1}{2}\left[h + \frac{0.0105}{3}\right](0.9188 - 0.0110)\ 931 \times 0.0105$$

or $h = 3.46$

Thus, liquid rises to a height of 3.46 cm in the capillary.

(*ii*) **The drop-weight method.** This method is mainly employed to compare the surface tensions of two liquids.

In this method, the liquid whose surface tension is to be determined, is allowed to pass drop by drop through a capillary tube held vertically. Every drop coming out of the capillary tube grows spherically in size and attains some definite weight. When the weight of the drop becomes equal to the force of surface tension, acting along the circumference of the capillary tube, it falls.

The relationship between the weight of the falling drop (W) and surface tension (γ) is given by the expression

$$\gamma = \frac{W g}{2\pi r f} \qquad \ldots (4.22)$$

where f is equal to $\frac{r}{v^{1/8}}$, v being the volume of the drop and r its radius.

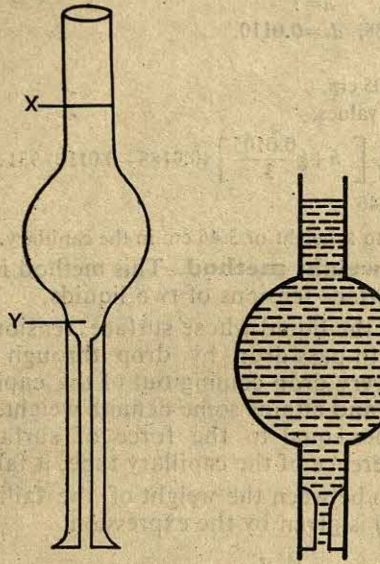
In actual practice, it is difficult to determine all the factors on the right hand side of equation (4.22). Thus, for convenience, surface tension of two liquids flowing separately through the same capillary tube, is compared.

If γ_1 is the surface tension of one liquid and γ_2 is the surface tension of another liquid, the two are related by the expression

$$\frac{\gamma_1}{\gamma_2} = \frac{W_1}{W_2} \qquad \ldots (4.22)$$

where W_1 and W_2 are the weights of drops of liquids 1 and 2 respectively.

The instrument used for the purpose is known as the stalagmometer and consists of a bubbled capillary tube as shown in the Fig. 4.9. The tube, after it has been thoroughly washed and dried, is filled by sucking upto some certain mark *A* with the liquid whose surface tension is to be determined. The liquid is then allowed to fall very slowly in the form of drops which are collected in a weighing bottle. The number of drops falling at the rate of one to two seconds is counted and their weight is determined. If W_1 and W_2 are the mean weights of drops of the two liquids and γ_1 and γ_2 are their surface tensions respectively, they are related to each other by equation (4.22).



(*a*) (*b*)

Fig. 4.9. (*a-b*) Stalagmometer.

It is more convenient to determine the number of drops formed by a definite volume of a liquid than to determine the weight of the drop.

Let n_1 and n_2 be the number of drops of equal volumes (say V) of two liquids 1 and 2 of densities d_1 and d_2 respectively.

The mean weight of drops of liquid 1 is given by

$$W_1=\frac{V}{n_1}\times d_1 \qquad \ldots (4.23)$$

and the mean weight of drops of liquid 2 is given by

$$W_2=\frac{V}{n_2}\times d_2 \qquad \ldots (4.24)$$

($\because$ weight of drop = volume of drop × density)

Therefore, equation (4.22) becomes

$$\frac{\gamma_1}{\gamma_2}=\frac{W_1}{W_2}=\frac{\frac{V}{n_1}\times d_1}{\frac{V}{n_2}\times d_2}$$

or

$$\frac{\gamma_1}{\gamma_2}=\frac{d_1 n_2}{d_2 n_1} \qquad \ldots (4.25)$$

From equation (4.25), knowing the surface tension of one liquid, usually called the reference liquid, the surface tension of the other liquid can be calculated simply by knowing their densities and the number of drops formed by the equal volume of the two liquids.

(*iii*) **The Tensiometric or Torsion balance method.** In this method, a platinum ring about 4 cm in circumference is immersed in the liquid to be tested from the end of the beam of a torsion balance and the force required to separate the ring from the surface of the liquid is then measured. The force f, required for this separation, is related to the surface tension of the liquid by the expression

$$f=\gamma\times 2(2\pi r) \qquad \ldots (4.26)$$

where $(2\pi r)$ is the circumference of the ring of radius r. The factor 2 is introduced because the force due to surface tension is acting at both the inner and the outer circumference of the ring.

From equation (4.26),

$$\gamma=\frac{f}{4\pi r} \qquad \ldots (4.27)$$

So knowing f and r, γ can be easily calculated.

This is the quickest method for determining the surface tension of a liquid and requires only small amounts of liquid.

TABLE 4.1

Surface tension of liquids at 20°C.

Liquid	$\gamma/(10^{-3}N/m)$	*Liquid*	$\gamma/(10^{-3}N/m)$
Acetone	23.70	Ethyl Ether	17.01
Benzene	28.85	n-Hexane	18.43
Carbon tetrachloride	26.95	Methyl alcohol	22.61
Ethyl acetate	23.90	Toluene	28.50
Ethyl alcohol	22.75	Water	72.75

Problem 4.6. In the determination of surface tension of a liquid, *A*, by the drop weight method using a stalagmometer, *A* gave 55 drops while water gave 25 drops; volume of the two liquids being the same. The densities of water and *A* are 0.996 and 0.800 gm/cm³ respectively and the surface tension of water is 72.0 dynes/cm. What is the surface tension of *A*?

Solution.

Since $\frac{\gamma_1}{\gamma_2}=\frac{d_1n_2}{d_2n_1}$

Here $\gamma_2=72.0$ dynes/cm

$d_2=0.996$

$n_2=25$

$\gamma_1=?$

$d_1=0.800$

and $n_1=55$ drops

Substituting these values in the equation, we have

$$\gamma_1=72\times\frac{0.800\times25}{0.996\times55}=26.3.$$

Therefore, surface tension of liquid $A=26.3$ dynes/cm.

Variation of surface tension with temperature. The surface tensions of all liquids decrease with increasing temperature and become zero at the critical temperature because at the critical temperature, there is no surface of separation between the liquid and the vapors. To represent the variation of surface tension of a liquid with temperature, many equations have been proposed. Some of them are given below:

(*i*) **Eötvös equation** (1886). According to this equation,

$$\gamma\left(\frac{M}{d_c}\right)^{2/3}=K(t_c-t) \qquad \ldots (4.28)$$

where γ is the surface tension of the liquid at temperature T and K is a constant independent of temperature. M, d_t and t_c are the molecular weight, density and the critical temperature of the liquid. Since $\left(\frac{M}{d_l}\right)$ is the molar volume, the factor $\left(\frac{M}{d_l}\right)^{2/3}$ is proportional to the molar surface area of the liquid and the product, $\gamma\left(\frac{M}{d_l}\right)^{2/3}$ gives the molar surface energy.

From equation (4.28), molar surface energy varies with temperature in a linear manner and becomes zero at the critical temperature.

(*ii*) **Ramsay-Shields equation** (1893). The equation proposed by W. Ramsay and J. Shields, is a modification over the Eötvös equation and is expressed as:

$$\gamma\left(\frac{M}{d_l}\right)^{2/3}=(t_c-t-6) \qquad \ldots (4.29)$$

This equation holds good for many liquids. According to this equation, γ will be zero at a temperature 6° below the critical point and will become negative at the critical point.

(*iii*) **Katayama's equation.** Katayama replaced (t_c-6) by t_c in the Ramsay-Shields equation to obviate the difficulty that γ is zero at

$t=t_c-6$ and proposed the following equation

$$\gamma\left(\frac{M}{d_l-d_v}\right)^{2/3}=K(t_c-t) \qquad \ldots (4.30)$$

where d_v is the density of vapor above the liquid at temperature t.

(*iv*) **MacLeod's equation (1923).** The equation is

$$\gamma=C(d_l-d_v)^4 \qquad \ldots (4.31)$$

where d_l is the density of the liquid and d_v is the density of the vapors—both measured at the same temperature. C is a constant, characteristic of each liquid but is independent of temperature.

This equation holds good with accuracy over a large temperature range for liquids which do not associate or dissociate.

In equations (4.28), (4.29) and (4.30), the value of the constant, K, was found to be 2.12 for all liquids that behave normally. However, those liquids such as water, alcohol, carboxylic acids etc., which are associated, gave not only abnormally low values of K but also showed variation of K with temperature. For some liquids which dissociate, the value of K was found to be higher than 2.12.

Interfacial tension. The surface tension measured against another immiscible or partially miscible liquid is referred to as interfacial tension. Consider two immiscible liquids A and B in contact with each other. If γ_A and γ_B are their respective surface tensions, then the interfacial tension γ_{AB} exists at the boundary between the two layers. Interfacial tension can be measured by the same methods that are employed for determining the surface tension of the pure liquids. For instance, in the drop weight method, the drops of the liquid may be counted in the liquid against which the interfacial tension is to be measured. The interfacial tension value γ_{AB} is generally intermediate between the surface tensions of the two liquids, γ_A and γ_B. It is given by $\gamma_{AB}=\gamma_A-\gamma_B$. Sometimes interfacial tension may be lower than the surface tension of the either liquid. For example, at 20°C, the surface tensions of water and carbon tetrachloride are 72.75 and 26.8 respectively. Their interfacial tension is equal to 45.0, which is very nearly equal to the difference of their surface tensions. But in the case of water and ethyl ether, the interfacial tension at 20°C is 10.7 which is lower than the surface tensions of water and ethyl ether at the same temperature (surface tensions of water and ethyl ether at 20°C are 72.75 and 17.0 respectively.) The phenomena of interfacial tension is of considerable importance in connection with the properties of emulsions, detergents, foams etc.

Problem 4.7. From the following data

t°C	dt gm/cm^3	γ dynes/cm
0°C	0.927	4.5
20°C	0.772	1.16

Calculate t_c for carbon dioxide using Ramsay equation.

Solution. According to Ramsay equation

$$\gamma\left(\frac{M}{dl}\right)^{2/3}=K\,(t_c-t-6)$$

$$M=44$$

Substituting the various values from the data at 0°C (273.16 K)

$$4.5\left(\frac{44}{0.927}\right)^{2/3}=K[t_c-(273.16+6)]$$

or

$$140.85=K(t_c-279.16)$$

Similarly, substituting the various values at 20°C (293.16 K)

$$1.16\left(\frac{44}{0.772}\right)^{2/3}=K[t-_c(293.16+6)]$$

or

$$36.31=K[t_c-(299.16)]$$

Taking the ratio of the two equations,

$$\frac{140.85}{36.31}=\frac{(t_c-279.16)}{(t_c-299.16)}$$

or

$$t_c=306.1\text{ K}$$

$$=33°\text{C}.$$

4.4. VISCOSITY OF LIQUIDS

All liquids exhibit a certain resistance or opposition to flow known as viscosity. The viscosity results due to the internal frictional forces of the liquid. Since in every liquid, there are strong attractive cohesive forces between the various molecules, therefore, when a layer is moving faster than the other layer, then due to the strong attractive forces, there is slowing down of the faster layer.

Consider the laminar flow of a river. It is observed that the layers of water adjacent to the banks of a river are stationary. But as the distance from the banks increases, the velocity of flow of water also increases and becomes maximum at the centre of the river. Now a layer which is moving slowly will try to slow down the motion of the adjacent layer and thus there will be some sort of frictional force between the two layers.

The frictional force, f, opposing the relative motion of two adjacent layers is

$\propto S$ (the area of interface between the two liquid layers)

and $\propto \frac{dv}{dx}$ (velocity gradient).

On combining the two,

$$f\propto S\,\frac{dv}{dx}$$

or

$$f=\eta\,S\,\frac{dv}{dx} \qquad \ldots(4.32)$$

where η is a proportionality constant known as the *coefficient of viscosity.* This is characteristic of each liquid and decreases with

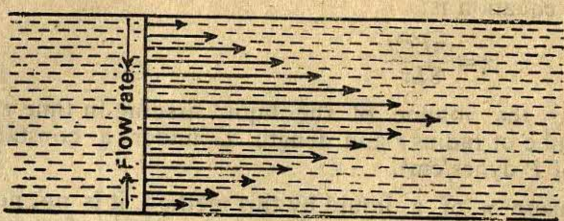


Fig. 4.10. Flow rate in a river.

increase of temperature.

Equation (4.32) can also be written as

$$\eta=\frac{f/S}{dv/dx} \qquad \ldots (4.33)$$

From this equation, coefficient of viscosity can be defined as the force in dynes per unit area required to maintain a unit difference of velocity between two parallel layers of a liquid, one centimetre apart.

If the coefficient of viscosity is high, the liquid does not rapidly flow and is viscous, for example, glycerine, honey, etc. But, if coefficient of viscosity is small, the liquid flows easily, for example, water.

Units of η

$$\because \eta=\frac{f/S}{dv/dx}=\left(\frac{\text{dynes}}{\text{cm}^2}\right)\times\frac{1}{(\text{cm/sec})}\times\frac{1}{(1/\text{cm})}=\text{dynes cm}^{-2}\ \text{sec}^{-1}$$

=poise.

When a force of one dyne can maintain a velocity difference of one centimetre per second between two adjacent layers of a liquid, one centimetre apart and having an area of interface one square centimetre, the liquid is considered to have a coefficient of viscosity of one poise.

(Poise is from the name of Poiseuille who originated the idea of viscosity.)

The SI units of viscosity is Newton second per square metre ($Nms^{-2}O$). This is also 1 Pascal second (1 Pas).

Determination of Coefficient of Viscosity

There are two methods which are generally employed to determine the coefficient of viscosity of a liquid. These methods are based on either the Poiseuille equation or Stokes equation.

(*i*) **Method based on Poiseuille equation**. Poiseuille in 1842 gave an equation that gives the relationship between the coefficient of viscosity and rate of flow of a liquid through a long and thin tube. The equation is

$$\eta=\frac{\pi Pr^4t}{8Lv} \qquad \ldots (4.34)$$

where v is the volume of the liquid issuing in time t through a capillary tube of radius r and length L under a constant driving pressure of P dynes/cm^2.

To measure η of a liquid by this method, it is not necessary to determine all the quantities on the right hand side of equation (4.34). We measure the viscosity of one liquid relative to some other reference liquid, generally water whose coefficient of viscosity has been determined accurately. The usual procedure is to determine the time of flow of fixed volume of two different liquids through the same capillary tube and then compare the two time flow.

If η_1 and η_2 are the coefficient of viscosities of two different liquids of densities, d_1 and d_2 respectively and t_1 and t_2 are the times of flow of the same volume (say v) of the two liquids, then from Poiseuille's equation

$$\eta_1=\frac{\pi P_1r^4t_1}{8Lv}$$

and $$\eta_2=\frac{\pi P_2r^4t_2}{8Lv}$$

where P_1 and P_2 are the pressures on the liquids 1 and 2 respectively.

Taking the ratio of the two equations

$$\frac{\eta_1}{\eta_2}=\frac{t_1P_1}{t_2P_2} \qquad \ldots (4.35)$$

But, since pressure $\propto$ density of the liquid,

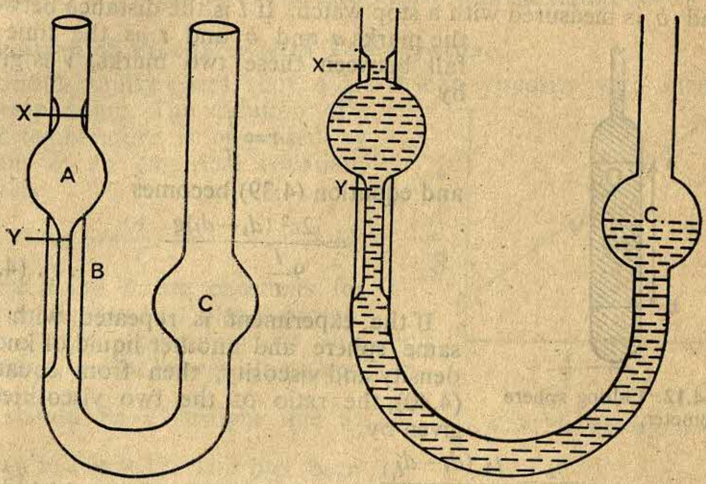
$$P_1 \propto d_1 \text{ and } P_2 \propto d_2$$

$\therefore$ Equation (4.35) becomes

$$\frac{\eta_1}{\eta_2}=\frac{t_1d_1}{t_2d_2} \qquad \ldots (4.36)$$

From equation (4.36), η_1 can be calculated if η_2, d_1 and d_2 are known and t_1 and t_2 determined.

The times t_1 and t_2 are easily measured with the help of an instrument known as *Viscometer*. A simple form of viscometer designed by Ostwald is shown in Fig. 4.11. A definite volume of the liquid whose coefficient of viscosity is to be determined is introduced into bulb C. It is then drawn up by suction into the bulb A and the time taken by the liquid to flow between the marks x and y is accurately measured with the help of a stop watch. The viscometer is then thoroughly cleaned, the other liquid of known viscosity is introduced and the whole operation is repeated. The viscometer is always placed in the thermostat to maintain constant temperature. Knowing t_1 and t_2, coefficient of viscosity of the liquid is calculated from equation (4.36).



a *b*

Fig. 4.11(*a-b*). Ostwald Viscometer.

(*iii*) **Method based on Stoke's equation**. Stoke's law deals with the fall of a solid body through a liquid. When a spherical body of radius r and density ds falls under gravity through a liquid of density d_l, it is acted on by the gravitational force, f_1 given by

$$\begin{aligned} f_1 &= \text{weight of spherical body} - \text{weight of liquid displaced} \\ &= \tfrac{4}{3}\pi r^3 \times d_s \times g - \tfrac{4}{3}\pi^3 \times d_l \times g \\ &= \tfrac{4}{3}\pi r^3 (d_s - d_l) g \qquad \ldots (4.37) \end{aligned}$$

The body falling under the gravitational force is opposed by the frictional forces within the liquid. Hence it does not fall with a continued increase of velocity. The body acquires a constant velocity, called the *terminal velocity* when the gravitational force, f_1, with which the body falls is just balanced by the frictional force, f_2, acting upwards, f_2 is given by

$$f_2 = 6\pi r \eta v \qquad \ldots (4.38)$$

where v is the terminal velocity and η the coefficient of viscosity.

At equilibrium, $f_1 = f_2$

From equations (4.37) and (4.38),

$$\tfrac{4}{3}\pi r^3 (d_s - d_l) g = 6\pi r \eta v$$

or

$$\eta = \frac{2r^2 (d_s - d_l) g}{9v} \qquad \ldots (4.39)$$

Equation (4.39) is known as the Stoke's equation, and is the basis of the falling sphere viscometer which is shown in Fig. 4.12. The liquid whose coefficient of viscosity is to be determined is filled in the viscometer tube *V*. A small steel ball is then passed through the neck of the tube and the time taken by it to fall between the marks *a* and *b* is measured with a stop watch. If *l* is the distance between the marks *a* and *b* and *t* is the time of fall between these two marks, *v* is given by

$$v=\frac{l}{t}$$

and equation (4.39) becomes

$$=\frac{2r^2(d_s-d_l)g}{9\frac{l}{t}} \qquad \dots (4.40)$$

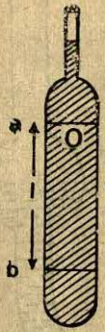


Fig. 4.12. Falling sphere viscometer.

If the experiment is repeated with the same sphere and another liquid of known density and viscosity, then from equation (4.40), the ratio of the two viscosities is given by

$$\frac{\eta_1}{\eta_2}=\frac{t_1(d_s-d_{l_1})}{t_2(d_s-d_{l_2})} \qquad \dots (4.41)$$

where d_{l_1} and d_{l_2} are the densities of the two liquids.

Thus knowing viscosity of one liquid and the times of fall of the same ball through two different liquids of known densities, the relative viscosity of the other liquid under study is easily calculated.

The ratio $\frac{\eta_1}{\eta_2}$, calculated from equation (4.41) or (4.42) is known as the relative viscosity of liquid 1 with respect to liquid 2.

Viscosities measurements of solutions of polymers are normally utilised to determine the molecular weight of polymers. If η is the viscosity of a solution at concentration *c* and η_o is the viscosity of pure solvent, then the ratio $\frac{\eta-\eta_o}{\eta_0}$ is known as the specific viscosity (η_{sp}) of the solution is defined as

$$\frac{\eta-\eta_o}{\eta_o}=\eta_{sp} \qquad \dots (4.42)$$

η_{sp} is found to vary with concentration in an approximately linear manner and the function $\frac{\eta_{sp}}{c}$ is nearly constant. The value $\left(\frac{\eta_{sp}}{c}\right)_{c\to o}$, obtained by extrapolating a plot of $\frac{\eta_{sp}}{c}$ against concentration to zero concentration, is known as the intrinsic viscosity, $[\eta]$.

Fluidity (ϕ). This is the reciprocal of viscosity *i.e.*

$$\phi=\frac{1}{\eta} \qquad \text{. . . (4.43)}$$

Fluidity is a measure of the ease with which the liquid flows.

Variation of Viscosity with Temperature

Liquids, unlike gases, show a decrease in viscosity with increase in temperature. The variation of η with temperature is expressed by means of an empirical equation, namely

$$\log \eta=\frac{A}{T}+B \qquad \text{. . . (4.43)}$$

where A and B are constants for a given liquid and T is the absolute temperature. According to this equation, a plot between $\log \eta$ and $\frac{1}{T}$ should be a straight line as shown in Fig. 4.13. This has been verified for a large number of pure liquids.

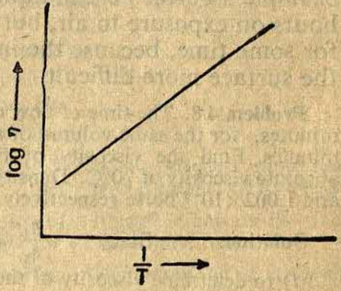


Fig. 4.13. Plot of $\log \eta$ *vs* $\frac{1}{T}$.

The viscosity of liquids has been found to decrease for each degree rise in temperature. The viscosities of a few liquids at temperatures are given in Table 4.2.

TABLE 4.2.
Viscosities of Some Liquids (millipoise)

Liquids	*0°C*	*20°C*	*25°C*	*30°C*
Acetic acid		12.22	11.60	10.40
Acetone	4.01	3.31	3.16	2.95
Benzene	9.0	6.50	—	5.61
Carbon Tetrachloride	13.40	9.70	—	8.45
Chloroform	7.00	6.25	5.60	5.10
Ethyl alcohol	17.73	12.00	—	10.03
Methyl alcohol	8.10	5.93	5.47	5.10
Toluene	7.72	5.90	—	5.26
m-Xylene	8.06	6.20	—	4.97
o-Xylene	11.05	8.10	—	6.27
p-Xylene	—	6.48	—	—
Hexane	20.5	18.4	17.90	—

Uses of Viscosity

Viscosity finds numerous applications in the field of chemistry, biochemistry and pharmacy. Lubricants are graded according to their viscosities. The measurement of viscosity of colloidal solutions may provide some evidence of the molecular weight of the particles. The technique is employed to a considerable extent in the study of colloid systems, because the experimental method is relatively simple.

The viscosity of a liquid or solution affects the rate at which the sensitive components can suffer oxidation at the liquid surface. For example ascorbic acid in aqueous solution is decomposed in a few hours on exposure to air, but in the form of syrup it may be preserved for some time, because the increased viscosity makes access to air at the surface more difficult.

Problem 4.8. The time of flow of water through an Ostwald viscometer is 1.52 minutes, for the same volume of an organic liquid of density 0.800 g/cc, it is 2.25 minutes. Find the viscosity of the liquid relative to that of water and also absolute viscosity at 20°C. Density and viscosity of water at 20°C are 1 gram/cc and 1.002×10^{-2} poise respectively.

Solution. Since $\frac{\eta_1}{\eta_2} = \frac{t_1 d_1}{t_2 d_2}$

(*i*) to determine viscosity of the liquid relative to that of water,

Here $t_1 = 1.52$ min., $d_1 = 1.0$ gram/c.c.,

$t_2 = 2.25$ and $d_2 = 0.800$ gm/c.c.,

$$\therefore \quad \frac{\eta_1}{\eta_2} = \frac{1.0 \times 1.52}{0.8 \times 2.25} = \frac{1.52}{1.8} \text{ or } \frac{0.844}{1.0}$$

or $\eta_1 : \eta_2 :: 0.844 : 1.0$

(*ii*) to determine absolute viscosity at 20°C.

Since viscosity of water at 20°C $= 1.002 \times 10^{-2}$ poise

$$\eta_1 = \eta_2 \frac{d_1 t_1}{d_2 t_2}$$

η_1 = viscosity of liquid

η_2 = viscosity of water

$$= \frac{1.002 \times 10^{-2} \times 0.8 \times 2.25}{1.0 \times 1.52}$$

$$= 1.187 \times 10^{-2} \text{ poise.}$$

Problem 4.9. A steel ball of density 7.99 gram/c.c., and a diameter of 4 mm requires 53 seconds to fall a distance of 1 metre through an oil of density 1.10 gm/c.c. Calculate the viscosity of oil in poise.

Solution. $\eta = \frac{2r^2(d_s - d_l)g}{9\, l/t}$

Here $r = 0.2$ cm., $d_s = 7.99$ gram/c.c.

$d_l = 1.10$ gram/c.c., $l = 100$ cm.,

$t = 53$ seconds and $g = 980$

Substituting the various values,

$$\eta = \frac{2 \times (0.2)^2 (7.99 - 1.1)\, 980}{9 \times 100/53}$$

$$= 31.39 \text{ poise.}$$

PROBLEMS

1. Explain the following:
   (*a*) Gases are more compressible than liquids.
   (*b*) The effect of temperature on the condensation of a gas.

(*c*) The effect of pressure on condensation of a gas.

(*d*) Liquids diffuse very slowly.

2. At 25°C, 10 litre of dry air is bubbled slowly through 115.2 g. of a pure liquid whose molecular weight is 420 g/mol. The remaining liquid weighed 113.1 g. Assuming the vapor to behave ideally and the volume to be approximately equal to that of the dry air, calculate the vapor pressure of the liquid.

Ans. 0.043 atm.

3. (*a*) Would molecules with high mutual attractions be expected to have a high or low vapor pressure? Why?

(*b*) The equilibrium vapor pressures at 20°C for some of the compounds are listed below:

	Vapor pressure
H_2O	17.5 mm Hg
CCl_4	91.0 mm Hg
$CHCl_3$	160.0 mm Hg

which compound has the least and which compound has the greatest molecular attraction?

Ans. H_2O greatest; $CHCl_3$ least.

4. What do you understand by surface tension of a liquid? What are its units and dimensions? Give one experimental method for its determination.

5. What do you understand by interfacial surface tension? How is it determined experimentally?

6. A capillary tube of radius 0.01 cm. is dipping through in a two-layer system consisting of water and benzene, the liquid meniscus rises by 4 cm. Calculate the interfacial tension between water and benzene. Given that the glass-water-benzene contract angle is 40° and the densities of water and benzene are 1.00 and 0.80 respectively.

Ans. 5.1 dyne/cm.

7. Define parachor and discuss its use in the elucidation of molecular structure.

8. Define coefficient of viscosity. How does it vary with temperature?

9. Give one method for the determination of viscosity of a liquid.

10. Write short notes on the following:

(*a*) Boiling point of a liquid.

(*b*) Trouton's rule.

(*c*) Intrinsic viscosity.

11. Select the term that is best associated with each of the following definitions, description or specific examples.

(A) distillation (B) immiscible (C) surface tension (D) viscosity.

(*a*) not mutually soluble.

(*b*) resistance to flow.

(*c*) can be measured by a capillary rise method.

(*d*) boiling followed by condensation.

Ans. (*a*) (B) (*b*) (D) (*c*) (C) (*d*) (A).

12. The surface tension of water is 7.28×10^{-2} Nm^{-1} at 20°C and 5.89×10^{-2} Nm^{-1} at 100°C. The densities are respectively 0.998 g cm^{-3} and 0.958 g cm^{-3}. To what height will water rise in tubes of internal radius (*a*) 1 mm (*b*) 0.1 mm?

Ans. (*a*) 1.49 cm (*b*) 1.25 cm

13. A glass tube of internal diameter 1.00 cm surrounds a glass rod of diameter 0.98 cm. How high will water rise in space between them?

14. Calculate the surface tension of a solution of wetting agent which has a density of 1.008 g/cm^3 and which rises 6.60 cm in a capillary tube having an inside radius of 0.02 cm.

Ans. 65.2 dynes/cm.

Chapter 5

THE SOLID STATE

5.1. INTRODUCTION

Crystals are objects of wonder. They have fascinated man since earliest times and their use almost certainly predates recorded history. They served as ornaments, medicines and tools. In more advanced societies crystals have more sophisticated uses such as for lenses, curios and even windows. We live in a world of crystalline materials. The colors of wall paint and gemstones, the texture of fudge and ice cream, the strength of bridge cables, the shapes of gallstones and hailstones, the hardness of diamond and the shiny appearance of metals are all determined by crystallographic properties. It is important to differentiate, natural, synthetic and imitation crystals. Natural crystals are found in nature—in rock beds, loose sediments and natural waters. These crystals are of minerals which are naturally occurring chemical compounds with a characteristic crystal structure and a composition that varies within defined limits. Synthetic crystals are manufactured from simple or complex components. The word synthesis literally means "put together." Thus a synthetic gemstone can be chemically, physically and structurally identical to natural counterpart. The only difference is that the synthetic was made by man, rather than by nature. Identification of a synthetic is possible only because the growth method generally introduces characteristic defects, inclusions or other visible features.

An imitation is a material with properties that mimic those of a different more costly material. Thus red glass is widely used imitation ruby. Synthetic ruby, however, is not an imitation.

Crystals are of immense importance to man. Most watches contain a number of "jewels"; they are made of synthetic ruby. Portable radios and TV sets, minaturised hearing aids, auto ignitions, telephone systems and thousands of other devices contain "solid state" components small chips of single crystals with a complex fabrication history. Man made crystals are so important that without them civilisation as we know it would not be possible.

5.2. CRYSTALLINE STATE

It was thought until recently that all solids were crystalline and that there were no truly amorphous solids. Riby has shown that the solid state must include both crystalline and amorphous substances.

A crystalline solid is characterised by the three criteria:

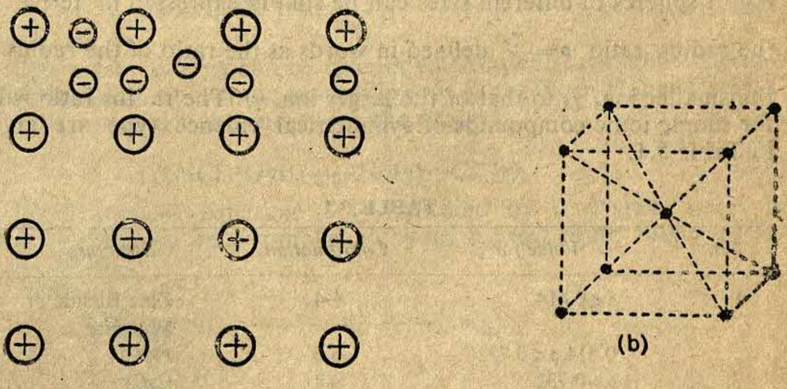
(*i*) a definite melting point,
(*ii*) a definite heat of fusion, and
(*iii*) a definite crystal lattice.

However, it is not always possible to tell by the external appearance alone whether a substance is crystalline or amorphous. Many substances when ground to a fine powder appear to be amorphous; but examination under a microscope will show the structure to be crystalline. The substances which are rigid but do not conform to the above requirements are called “amorphous solids. ”The examples of amorphous solids are glass, rubber and solid glue. The term amorphous has been adopted from the Greek and means “shapeless” *i.e.*, the substance has no natural geometrical form or a regular internal structure. The particles of the amorphous substance are arranged at random as in a liquid. Therefore, solid amorphous substances are regarded as supercooled liquids.

All our discussions of crystal structure shall be based on an abstraction called a “perfect crystal.” A perfect crystal is one in which the structure is perfectly periodic. In actual practice, crystals are never perfectly periodic and the reasons for deviations from the ideal behaviour are (1) the finite extent of crystals, (2) the existence of structural defects.

5.3. TYPES OF SOLIDS

On the basis of the nature of forces that hold the particles together,


(a)
(b)

⊕ indicates the centre of a sodium ion.
⊖ indicates an electron.
⊙ indicates the centre of the sodium atom.

Fig. 5.1. Two representations of the structure of the sodium metal.

solids are classified into four main types: (*a*) metallic solids, (*b*) iodic solids, (*c*) covalent solids, and (*d*) molecular solids.

However, this classification is arbitrary, but provides a basis to understand the similarities and the differences in the various types of solids.

(*a*) **Metallic solids**. The properties like electrical conductivity, malleability and metallic lustre indicate that the metals possess some unique electronic structure and bonding. This is referred to as the metallic bond. Qualitatively one can assume in a metal, the positive ions being closely packed in a sea of electrons. The force of attraction between the metal ions and the electrons is responsible for cohesion in the metals. A metal can also be regarded as an assemblage of positive ions immersed in a gas of free electrons. These electrons are the valency electrons. The structure of the sodium metal is shown in Fig. 5.1. The attraction between the positive charge and the electron gas gives the structure its coherence and the free mobility of this electron gas under the influence of electrical or thermal stress is responsible for the high conductivity of metal.

(*b*) **Ionic solids**. Ionic solids are made up of positive and negative ions. The ions are held together by ionic bond resulting from the electrostatic interaction of oppositely charged ions. However, a smaller contribution results from the interaction of the charge of a given ion with the polarizability of the neighbouring ions. These electrostatic forces result in a completely non-directional pulling together of the units of the crystal. The structure, in the case of simple ions, can be understood in items of nothing more than the efficient packing together of two sets of spheres of different sizes.

Pauling has shown that the geometric requirements for close packing of spheres of different sizes can be simply expressed in terms of the radius ratio $\rho=\frac{\gamma_s}{\gamma_l}$ defined in words as the ratio of the radius of the smaller ion, γ_s to that of the larger ion, γ_l. The radius ratio rules for simple ionic compounds of symmetrical valence type are given in Table 5.1.

TABLE 5.1.

No.	*Value for* ρ	*Coordination*	*Structure*
1.	$\rho<0.414$	4-4	Zinc Blende or Wurtzite
2.	$0.414\ \rho<0.732$	6-6	NaCl
3.	$\rho>0.732$	8-8	CsCl

These rules enable us to predict satisfactorily the structure of the compound from the relative sizes of the two ions. The exceptions to the radius ratio rules may be due to two reasons (*a*) the ions are not rigid spheres, (*b*) the ions of opposite charges are not in contact.

Formation of an ionic solid. Consider a process whereby the gaseous ions, which are very far apart at the higher temperature, will condense upon cooling into an orderly three dimensional array in an ionic crystalline solid. The energy evolved when one mole of gaseous negative and positive ions are brought together into such a crystal is called the *crystal energy* or *lattice energy*. It has been found that the potential energy per pair of ions in a crystal latice is not the same as that of an isolated pair of ions in free space. When the mutual potential energies of all the ions in a crystal are summed up, the total energy E_T is given by

$$E_T=\frac{AZ_aZ_ce^2}{r_0}+\frac{B}{r^n} \qquad \ldots (5.1)$$

where Z_a and Z_c are the charges on the anion and cation respectively, e is the electronic charge, r is the separation of charges and A is a constant called Madelung constant. It is the geometrical correction factor and its numerical value depends upon the type of crystal structure. B is another empirical constant which is evaluated using the fact that the potential energy is a minimum when $r=r_0$, the internuclear separation in the crystal. When one mole of ions is considered, the equation (5.1) for the crystal energy E_T becomes,

$$E_T=\frac{NAZ_aZ_ce^2}{r_0}\left(1-\frac{1}{n}\right) \qquad \ldots (5.2)$$

where N is Avogadro's number.

When $Z_a=-Z_c=1$

Equation (5.2) takes the form,

$$E_T=\frac{NAe^2}{r_0}\left(1-\frac{1}{n}\right) \qquad \ldots (5.3)$$

The crystal energy can be calculated from the available thermochemical data of a cyclic process known as the Born-Haber Cycle.

Let us consider the energy for the process

$$\text{NaCl (cryst)}\longrightarrow \overset{+}{\text{Na}}(g)+\text{Cl}^-(g) \qquad \ldots (5.4)$$

The process of equation (5.4) indicated by a dashed arrow in Fig. 5.2 can also be accomplished by an indirect route indicated by solid arrows.

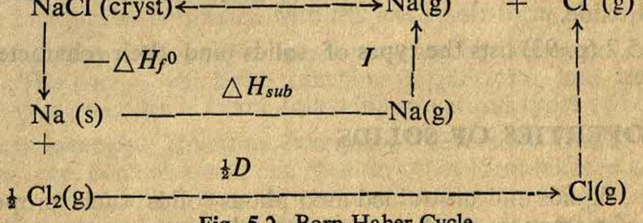


Fig. 5.2. Born-Haber Cycle.

The lattice energy ΔE(cryst) for sodium chloride can be written down as

$$\Delta E(\text{cryst}) = -\Delta H^0_f + \Delta H_{sub} + \tfrac{1}{2}D + I - A \quad \ldots (5.5)$$

where ΔH^0_f = standard heat of formation of NaCl

D = heat of dissociation of Cl_2

ΔH_{sub} = heat of sublimation of Na

A = electron affinity of Cl

and I = ionization potential of Na

The validity of theoretical crystal energy calculations cannot be directly checked since few independent electron affinity results are available. However, one can calculate the electron affinity of the chloride atoms from the data for NaCl, KCl and others. The fact that one gets the same electron affinity value within a few per cent for all these crystals indicates that the method is sound. The examples of ionic solids are NaCl, NaF, LiF and AgCl.

Problem 5.1. Calculate the lattice energy of cesium iodide which has an interionic distance of 3.95Å. The values of Madelung constant and Born exponent for CsI are 1.76 and 12 respectively.

Solution. The lattice energy E_T is given by

$$E_T = -\frac{ZaZcNAe^2}{r_0}\left(1-\frac{1}{n}\right)$$

$$= -\frac{(1)^2\,(1.76)(6.02)\times 10^{23})\,(4.8\times 10^{-10})^2}{3.95\times 10^{-8}}\left(1-\frac{1}{12}\right)$$

$$= -5.65\times 10^{12} \text{ ergs/mol}$$

or $E_T = -135$ k. cal/mol.

(*c*) **Covalent solids**. The covalent bond is the classical electron pair bond. Comparatively few solids are held together exclusively by covalent bond. A majority of solids incorporating the covalent bonds are also bound either by ionic or van der Waals forces. The examples of covalent solids are diamond, silicon carbide, zinc sulphide and silver iodide.

(*d*) **Molecular solids**. In molecular solids, the bonding capacity of both atoms is saturated and the molecule has no residual capacity for further bonding. It is because of the weak forces of attraction present in them, that they possess low melting and boiling points. These weak forces which originate from dipole-dipole induction and London dispersion forces are called van der Waals forces. The examples of molecular solids are graphite, mica, argon and carbon dioxide.

Table 5.2 (p. 93) lists the types of solids and their characteristic properties.

5.4. PROPERTIES OF SOLIDS

For gases, liquids and unstrained amorphous solids such properties as index of refraction, coefficient of thermal expansion, thermal and

TABLE 5.2.

Type	*Nature of bonding force*	*Properties*	*Examples*
Metallic	Positive ions in a sea of electrons held by electrical attraction between the positive ion and electron gas	High melting and boiling point. High thermal and electrical conductivity	Na, Cu, Sb and Au
Ionic	Coulombic and electrostatic forces of attraction	Brittle, high melting point and conducting	NaF, NaCl, AgCl, LiF and CsCl
Covalent	Sharing of electrons	Hard, non-conducting and high melting	C (Diamond) ZnS, SiC and AgI
Molecular	Dipole-Dipole and van der Waals	Low melting point, volatile and soft	C (graphite) mica. Argon and CO_2

electrical conductivity are all independent of direction. The same is true of substances crystallising in the regular system. Such substances exhibiting the same properties in all directions are said to be isotropic.

However, for substances crystallising in the other crystal systems, the above properties may vary according to the axis along which the observation, is made. Substances exhibiting directional differences in properties are said to be anisotropic. Solids also exhibit the phenomenon of polymorphism and isomorphism.

Polymorphism. Many chemically different solid substances exist only in a single solid crystalline form. However, quite often certain substances occur in more than one solid modification and undergo a change of crystalline form on heating or under pressure. The existence of a substance in more than one modification is known as polymorphism and the various modifications are known as Polymorphs. Carbon exists in the crystalline form as either diamond or graphite. Sulphur has been found to exist in a variety of solid modifications. Tin and silver iodide are the other common examples of substances exhibiting this phenomenon. Polymorphism occurring in elements is more commonly referred to as allotropy. A more stable polymorph is found to have less energy content and a lower vapor pressure as compared with the less stable form.

The allotropic forms of a substance can be converted into each other. The way in which the transition of one form into the other form takes place leads to the following to various types of allotropy:

Enantiotropy. This is an example of reversible transformation. In this type, conversion of one form in other form takes place at a definite temperature, known as the transition point. One form is stable below the transition temperature while the other is stable above it. Some examples of enantiotropy with transition temperatures are given below in the Table 5.3.

TABLE 5.3.

Substance	*Form*	*Transition temperature (°C)*
Sulphur	Rhombic $\rightleftharpoons$ Monoclinic	95.6
Tin	Grey $\rightleftharpoons$ White	18
	White $\rightleftharpoons$ Rhombic	202.8
Zinc	$\alpha \rightleftharpoons \beta$	174
	$\beta \rightleftharpoons \gamma$	322
Ammonium Chloride	$\alpha \rightleftharpoons \beta$	184.5
Silver Iodide	Hegagonal $\rightleftharpoons$ Regular	146.5
Silver Nitrate	Rhombic $\rightleftharpoons$ Rhombohedral	160
Mercuric Iodide	Tetragonal $\rightleftharpoons$ Orthorhombic	126

Monotropy. In this type, transformations are, however, which proceed at all temperatures in one direction and there is no definite transition temperature. Conversion of ozone into oxygen is a good example of monotropy. Thus ozone changes into oxygen at all temperatures, but a reversal of the process by which the change was started does not lead to the reformation of the ozone.

Dynamic allotropy. Here, two forms exist together in equilibrium *i.e.*, one form changes into the other form at exactly the same speed as the reverse process takes place. Examples of this type is liquid sulphur, which consists of a mixture of two forms of sulphur, represented as $S\nearrow$ and $S\mu$, which are in equilibrium with each other. These forms differ in molecular complexity.

Isomorphism. For quite long time many pairs of compounds of similar composition were known which would also crystallise in the same form and were said to be isomorphous. A set of common examples are

$$\begin{cases} Cu_2S \ KClO_4 \\ Ag_2S \ KMnO_4 \end{cases} \qquad \begin{cases} ZnSO_4.7H_2O \\ MgSO_4.7H_2O \end{cases}$$

and

$$\begin{cases} K_2SO_4 \ Al_2(SO_4)_3.24H_2O \\ K_2SO_4.Cr_2(SO_4)_3.24H_2O \end{cases}$$

A careful study of such isomorphous compounds led Mitscherlich to formulate the law of isomorphism known as Mitscherlich's Law of Isomorphism which states:

> "Substances possessing an equal number of atoms united in the same fashion have identical crystalline structure."

It led to the concept that the crystalline form depends upon the number of atoms and the method in which they are united and is independent of their chemical nature. From a detailed information of the structure of crystals, for any two substances to be isomorphous, following conditions must be fulfilled.

(*a*) The substances must be of the same formula type.

(*b*) The relative sizes of the constituent structural units should nearly be same.

(*c*) The stereochemical form of the radical units, if any, must be similar.

(*d*) The polarising properties of the structural units in the two substances should be almost equal.

5.5. CRYSTALLOGRAPHY

Crystallography is the science of crystals which deals with the study of their development and growth, their external form, internal structure and physical properties. It is based on three fundamental laws: (*a*) Steno's law of constancy of interfacial angles,

(*b*) Hauy's law of rationality of indices, and

(*c*) The law of symmetry.

(*a*) **The law of constancy of interfacial angles**. This law states that for a given substance, the corresponding faces or planes forming the external surface of a crystal always intersect at a definite angle and that this angle remains constant no matter, how the faces develop. Commonly it is observed that the crystal planes are unequally developed so as to produce the faces of variable size and shape; but the angle of intersection of any two corresponding faces is always found to be the same for any crystal of the same substance. The instrument employed for the measurement of interfacial angle is called Goniometer.

(*b*) **Hauy's law**. For any crystal, a set of three coordinate axes

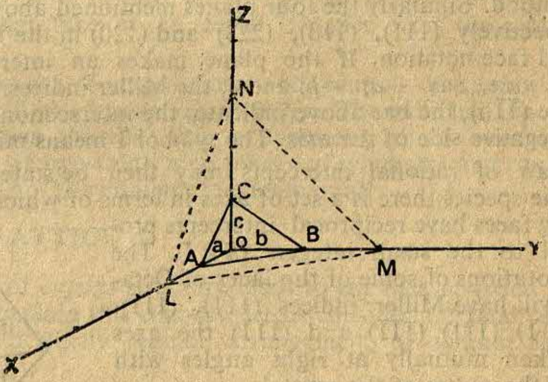


Fig. 5.3. Identification of Lattice planes by Miller indices.

can be chosen in such a way that all the faces of the crystal will either intercept these axes at definite distances from the origin or be parallel to some of the axis in which case the intercepts are at infinity. *See* Fig. 5.3.

The law of rationality of indices or intercepts proposed by Hauy, states that it is possible to choose along the three coordinate axes unit distances (*a*, *b*, *c*) not necessarily of the same length such that the ratio of the three intercepts of any plane in the crystal is given by $(ma : nb : pc)$ where *m*, *n* and *p* are either integral whole numbers including infinity or fractions of whole numbers.

Let us consider the crystals of mineral topaz, for which four different parameters have the following values:

(1) $m=1$ $n=1$ $p=1$
(2) $m=1$ $n=1$ $p=\infty$
(3) $m=1$ $n=1$ $p=\frac{2}{3}$
(4) $m=2$ $n=1$ $p=\infty$

and hence the intercept ratios are

(1) $a : b : c$
(2) $a : b : \infty c$
(3) $a : b : \frac{2}{3}c$
(4) $2a : b : \infty c$

For any particular plane these ratios characterise the plane and may be used to represent it. The coefficients of *a*, *b* and *c* are known as the Weiss indices of a plane. However, Weiss indices are rather awkward to use and have consequently been replaced by Miller's indices.

The Miller indices of a plane are obtained by taking the reciprocals of the Weiss coefficients and multiplying throughout by the smallest number that will express all the reciprocals as integers. Thus a plane in which the Weiss notation is given by $a : b : \infty c$ becomes in the Miller notation $a : b : 0c$ or simply (110) since the order *a*, *b*, *c* is understood. Similarly the four planes mentioned above for topaz are respectively (111), (110), (223) and (120) in the Miller system of crystal face notation. If the plane makes an intercept on the negative side, say $-a$; $-b$: and *c*, the Miller indices for the plane would be $(\bar{1}\bar{1}\bar{0})$, the bar above indicates the intersection of the plane on the negative side of the axis. The symbol $\bar{1}$ means minus unity.

The law of rational intercepts may then be stated as: for any crystalline species there is a set of axes in terms of which all natural occurring faces have reciprocal intercepts proportional to the small integers $(h\,k\,l)$. The Miller notations of some of the faces of Octahedron will have Miller indices (111), $(\bar{1}11)$, $(1\bar{1}1)$, $(11\bar{1})$, $(\bar{1}\bar{1}1)$, $(\bar{1}\bar{1}\bar{1})$ and $(\bar{1}\bar{1}\bar{1})$ the axes being taken mutually at right angles with origin of the centre of the crystal.

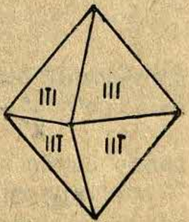


Fig. 5.4. The Octahedron with the front faces indexed.

(*c*) **The law of symmetry**. This law states that all crystals of the same substance possess the same elements of symmetry. Symmetry in crystals may be with respect to a plane, a line or a point. A crystal is said to have a *plane of symmetry* when it is divided by an imaginary plane into two halves such that one is the mirror image of the other.

A crystal possesses *a line of symmetry* when it is possible to draw an imaginary line through the centre of the crystal and then revolve the crystal about this line through 360° in such a way that the crystal appears unchanged more than once. In fact it is possible to have crystals which appear the same two, three, four or six times during one complete revolution of 360°. The line is called the *axis of symmetry*. Depending on the number of times a crystal appears unchanged on revolution is said to possess two, three, four and six fold axes of symmetry.

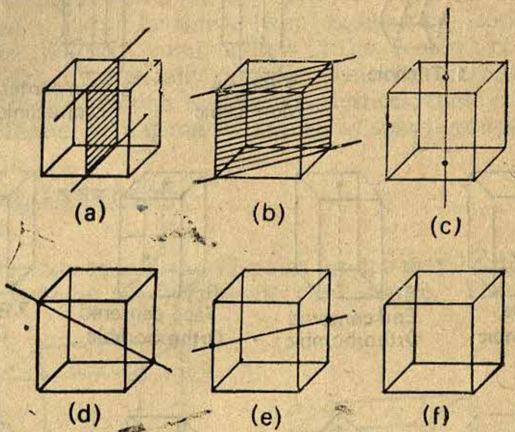


Fig. 5.5. Elements of symmetry of a cube.

A crystal is said to have a *centre of symmetry*, if every face has another identical face at an equal distance from the centre. *See* Fig. 5.5.

The total number of planes, lines and centres of symmetry of a crystal are called its *elements of symmetry*. The cube has the greatest symmetry. It has thirteen axes of symmetry (three four fold, four three fold and six two fold), nine planes of symmetry and one centre of symmetry, *i.e.*, 23 symmetry elements in all.

5.6. SPACE LATTICE

The regularity of crystal structure leads to the idea of space lattice. In order to explain this concept, let us consider a crystal of NaCl. It consists of a perfectly regular arrangement of sodium ions and chloride ions.

x . *x* . *x* . *x* .
. *x* . *x* . *x* . *x* . *x*
x . *x* . *x* . *x* .
. *x* . *x* . *x* . *x*
$x = Na^+$
. $= Cl^-$

Fig. 5.6. Space lattice of NaCl.

If we represent the position of each Na^+ in the crystal by a point (marked x), the result will be a regular three dimensional network

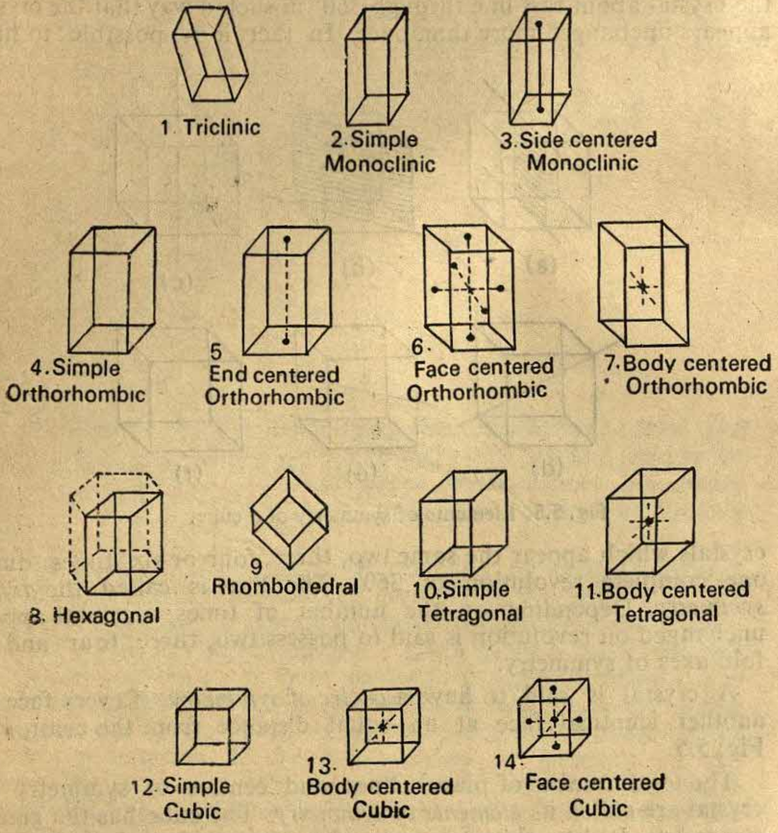


Fig. 5.7. The fourteen Bravaislattices.

of points. This will be the space lattice of Na^+ in the crystal of NaCl. Similarly, there will be a space lattice for Cl^- and the space lattice for NaCl is made up of the interpenetration of Na^+ and Cl^- lattices. The symmetry of the combined lattice determined the symmetry of the crystal as a whole. It may be noted that each lattice point in the lattice has exactly the same surroundings as any other point representing the same atom or iron. The space lattice of a crystal may be considered as built up of a three dimensional basic pattern called the *unit-cell*. The unit-cell is a repeat unit which will generate the whole pattern in three dimensions. The external appearance of the crystal is determined by the shape and dimensions of the unit cell. It can be proved by geometrical arguments that only fourteen different simple space lattice are possible, *See* Fig. 5.7.

These are called *Bravais* lattices. All the crystals in the cabic or a regular system are made up of one or more of three kinds of lattices, (*a*) the simple cube, (*b*) the face centered cube, and (*c*) the body centered cube. This is shown in Fig. 5.7 (12, 13, 14).

The actual lattice consists of a repetition of these units cells in three dimensions. It can be shown from geometrical considerations that thirty-two different combinations of the elements of symmetry of a crystal are theoretically possible. These are referred to as 32 point groups. In conjunction with Bravais lattices, these point groups lead to 230 different arrangements known as space groups.

5.7. CRYSTAL SYSTEMS

The 14 Bravais lattices and the 32 point groups may be divided into seven-crystal systems for practical convenience. These systems

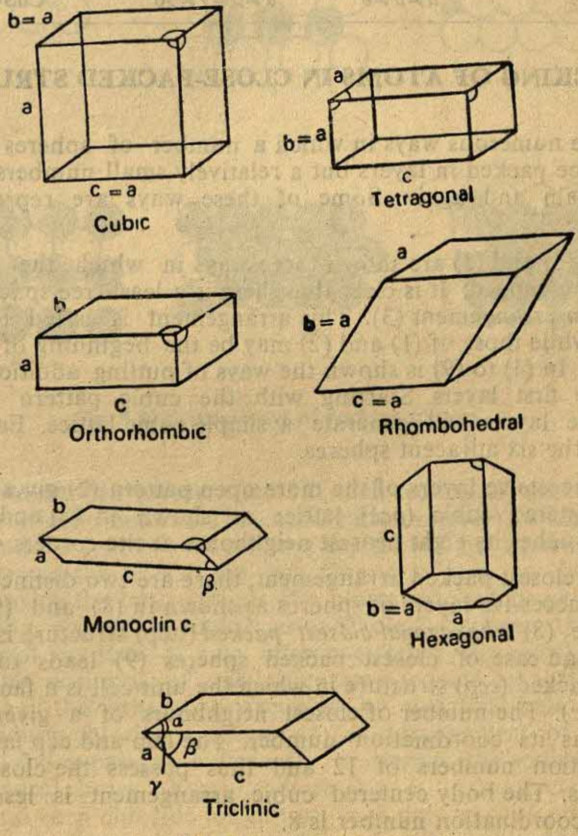


Fig. 5.8. Seven-crystal systems.

can be determined by symmetry considerations and the coordinate axes that are used. These are given in Table 5.4 and are shown in Fig. 5.8.

TABLE 5.4

The Crystal Systems

System	*Axes*	*Angles*	*Examples*
Cubic	$a=b=c$	$\alpha=\beta=\gamma=90°$	NaCl, Ag
Tetragonal	$a=b\neq c$	$\alpha=\beta=\gamma=90°$	White tin, MgF_2
Orthorhombic	$a\neq b\neq c$	$\alpha=\beta=\gamma=90°$	$HgCl_2$, Rhombic sulphur
Monoclinic	$a\neq b\neq c$	$\alpha=\gamma=90°$, $\beta=120°$	Monoclinic sulphur, $KClO_3$
Rhombohedral	$a=b=c$	$\alpha=\beta=\gamma\neq 90°$	Calcite, Al_2O_3
Hexagonal	$a=b\neq c$	$\alpha=\gamma=90°$, $\beta=120°$	Mg, Graphite
Triclinic	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq 90°$	$CuSO_4.5H_2O$

5.8. PACKING OF ATOMS IN CLOSE-PACKED STRUCTURES

There are numerous ways in which a number of spheres of equal size can be packed in layers but a relatively small numbers of these recur again and again. Some of these ways are represented in Fig. 5.9.

In (1), (2) and (3) are shown three ways in which the first layer might be arranged. It is clear that there is a least free space between spheres in arrangement (3). This arrangement is called the closest packed while those of (1) and (2) may be the beginning of the cubic patterns. In (4) to (9) is shown the ways of putting additional layers on these first layers. Starting with the cubic pattern of (1), the successive layers will generate a simple cubic lattice. Each sphere touches the six adjacent spheres.

The successive layers of the more open pattern (2) gives rise to a body centered cubic (*bcc*) lattice as shown in (5) and (8). Each sphere touches its eight nearest neighbours at the corners of a cube.

In the closest packed arrangement, there are two distinct ways of adding successive layers of spheres as shown in (8) and (9). In the first case (8) a *hexagonal closest packed* (hcp) structure is obtained. The second case of closest packed spheres (9) leads to the cubic closest packed (*ccp*) structure in which the unit cell is a face centered cube (*fcc*). The number of closest neighbours of a given sphere is known as its coordination number. The hcp and ccp lattices have coordination numbers of 12 and thus possess the closest packed structures. The body centered cubic arrangement is less compact and the coordination number is 8.

The packing of spheres in ionic solids is complicated by the fact that the ions are positively and negatively charged. In a lattice containing ions, it is geometrically impossible for any ion to have a

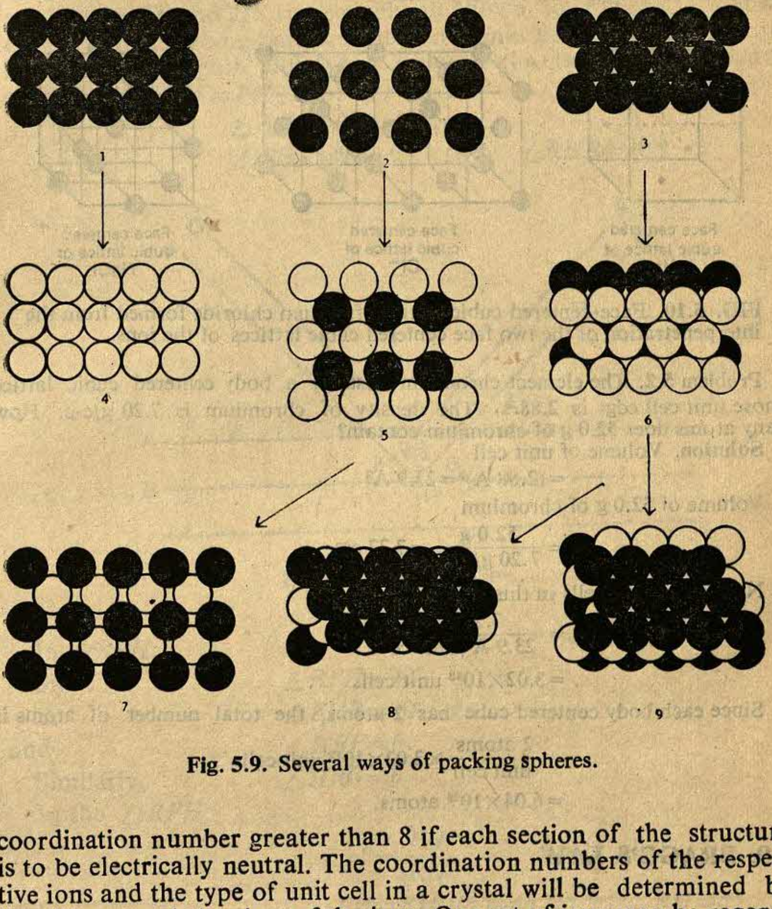
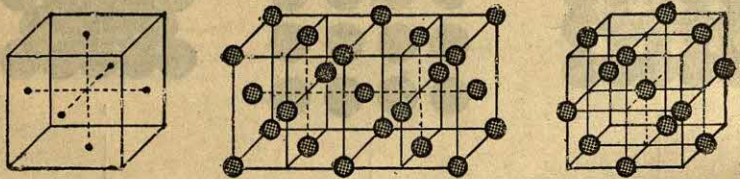


Fig. 5.9. Several ways of packing spheres.

coordination number greater than 8 if each section of the structure is to be electrically neutral. The coordination numbers of the respective ions and the type of unit cell in a crystal will be determined by the charges and the sizes of the ions. One set of ions may be regarded as occupying the lattice points of a closest packed structure while the other ions occupy the interstices or "holes" between them. The NaCl crystal consists of two interpenetrating close-packed (fcc) lattices. The positions of one lattice are occupied by positive ions, while those of the other are occupied by negative ions. We can imagine sodium chloride structure as fcc arrangement of chloride ions which has expanded sufficiently to permit the sodium ions in the octahedral holes. Every sodium ion is in contact with six chloride and each chloride ion in turn is in contact with six sodium ions; 6-6 coordination. The structure of sodium chloride is shown in Fig. 5.10.

We have discussed structures of metals and ionic crystals in terms of close-packed arrangement of spheres. If the particles are not spherical, the discussion will have to be done in a manner appropriate to the shape of the crystals.



Face centered cubic lattice of Na^+

Face centered cubic lattice of Cl^-

Face centered cubic lattice of NaCl

FIG. 5.10. Face-centered cubic lattice of sodium chloride formed from the interpenetration of the two face centered cubic lattices of the ions.

Problem 5.2. The element chromium exists as a body centered cubic lattice whose unit cell edge is 2.88Å. The density of chromium is 7.20 g/c.c. How many atoms does 52.0 g of chromium contain?

Solution. Volume of unit cell

$$=(2.88\ \text{A})^3=23.9\ \text{A}^3$$

Volume of 52.0 g of chromium

$$=\frac{52.0\ \text{g}}{7.20\ \text{g/c.c.}}=7.22\ \text{cm}$$

Number of unit cells in this volume

$$=\frac{7.22\ \text{cm}^3}{23.9\ \text{A}^3/\text{unit cc}}$$

$$=3.02\times10^{23}\ \text{unit cells}$$

Since each body centered cube has 2 atoms, the total number of atoms is

$$\frac{2\ \text{atoms}}{\text{unit cell}}\times3.02\times10^{23}\ \text{unit cells}$$

$$=6.04\times10^{23}\ \text{atoms.}$$

5.9. BRAGG'S LAW

W.H. Bragg and W.L. Bragg studied the diffraction of X-rays in detail. The diffraction of X-rays by crystals is a phenomenon of great importance to chemists since diffraction studies provide much structural information on the arrangement of atoms, ions or molecules in crystals. When monochromatic X-rays impinge upon the atoms in a crystal lattice, each atom acts as a source of scattering radiation of the same wavelength. The crystal acts as a series of parallel reflecting planes. Thus X-rays would be reflected according to the ordinary laws of reflections and the planes would reflect X-rays at all angles. The intensity of the reflected beam at certain angles will be maximum when the two reflected waves from two different planes have a phase difference equal to an integral multiple of the wavelength of X-rays while at some other angles the intensity of the reflected X-rays beam will be minimum.

Consider a beam of monochromatic X-rays of wavelength λ. It is incident on a crystal and, after reflection from the planes A and B, goes along RT and HS respectively as shown in Fig. 5.11. Let the crystal lattice spacing between the two planes be d and θ, the glancing angle. The path difference between the two reflected waves along RT and $HS = FH + HG$

$$\angle PHB = \theta$$

$$\therefore \quad \angle FHR = 90 - \theta \quad (\because \ \angle RHB = 90°)$$

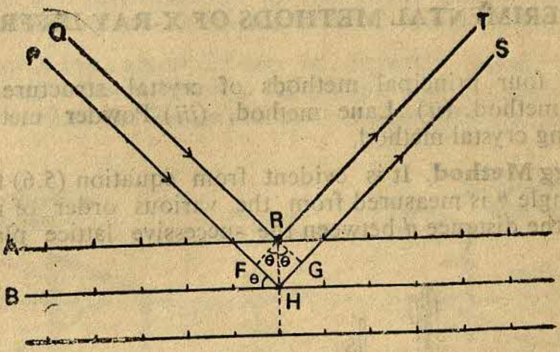


Fig. 5.11. Bragg's Law.

In $\triangle RFH$,

Since $\quad \angle RFH = 90°$

$\therefore \quad \angle FHR = 90° - \theta$

and $\quad \angle HRF = \theta$

Similarly, $\quad \angle HRG = \theta$

In the $\triangle RFH$,

$$\sin\theta = \frac{FH}{RH}$$

or $\quad FH = RH \sin\theta = d \sin\theta \ (\because \ RH = d)$

Similarly, $\quad HG = d \sin\theta$

$\therefore$ Path difference $\quad = FH + HG = 2d \sin\theta$

If the path difference between the two waves is an integral multiple of wavelength, the interference will be constructive as the reflected beams will reinforce each other. Therefore, for the reflected beam to be of maximum intensity.

$$2d \sin\theta = n\lambda \qquad \ldots (5.6)$$

where $\quad n = 1, 2, 3, 4, \ldots$

Equation (5.6) is known as Bragg's equation and represents Bragg's Law.

For $n=1$, we get,

$$2d \sin \theta = \lambda$$

This beam gives the spectrum of the first order. From the equation (5.6) it is clear that if the wavelength λ of X-rays which produces maximum intensity at a glancing angle θ is known, the distance between the atomic planes of a crystal, d, can be calculated. Similarly, if d is known, λ can be calculated.

In the X-ray studies it has become the standard practice to assume that all reflections are first order ($n=1$).

5.10. EXPERIMENTAL METHODS OF X-RAY DIFFRACTION

There are four principal methods of crystal structure analysis: (*i*) Bragg method, (*ii*) Laue method, (*iii*) Powder method, and (*iv*) Rotating crystal method.

(1) **Bragg Method**. It is evident from equation (5.6) that if the glancing angle θ is measured from the various order of maximum reflection, the distance d between the successive lattice planes of a given type in the crystal can be calculated. The positions of maximum reflection intensity can be determined using the Bragg X-ray spectrometer shown in Fig. 5.12.

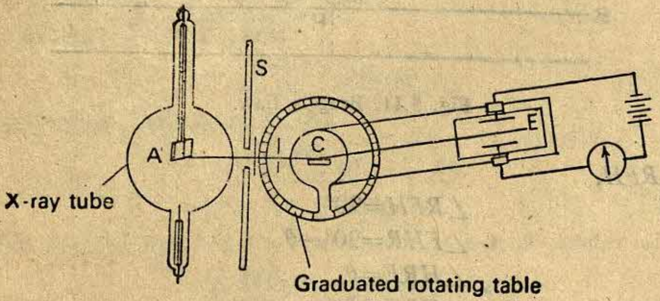


Fig. 5.12. Bragg X-ray Spectrometer.

A beam of X-rays of definite wavelength, coming from the anticathode A of an X-ray tube after passing through a slit S falls upon the face of the crystal (C) mounted on a rotating table. The rays after reflection from the crystal pass through another slit and are collected into a detector E of ionising radiation. Usually an ionization chamber or Geiger counter is employed for the purpose. The response of the detector is proportional to the intensity of entering X-rays. Starting with a small glancing angle between the incident X-rays and the crystal face, the value is increased in stages by rotating the table. The apparatus is so designed that the reflected ray always enters the detector chamber E and the intensities of the reflected X-rays for the various angles are determined. The glancing angles θ for which the strongest reflections are obtained are those which satisfy the Bragg equation. This procedure is repeated for all the important planes of the crystal. The X-ray spectrometer method of studying crystal structure requires the use of a relatively large crystal with well defined faces, and since reflections of several orders must be examined for number of faces, the total labour involved is large.

(2) **Laue Method.** In this case a single crystal is mounted with a given crystal axis perpendicular to the X-ray beam. The general arrangement of the apparatus used is shown in Fig. 5.13.

A beam of X-rays, about 0.5 mm in diameter, passes through a collimator and is then allowed to fall upon a crystal. After differaction by the crystal, the X-rays fall upon a photographic plate which records the positions and intensities of the diffracted rays. The Bragg equation $n\lambda = 2d \sin \theta$ must be satisfied for constructive interference of the diffracted X-rays to occur.

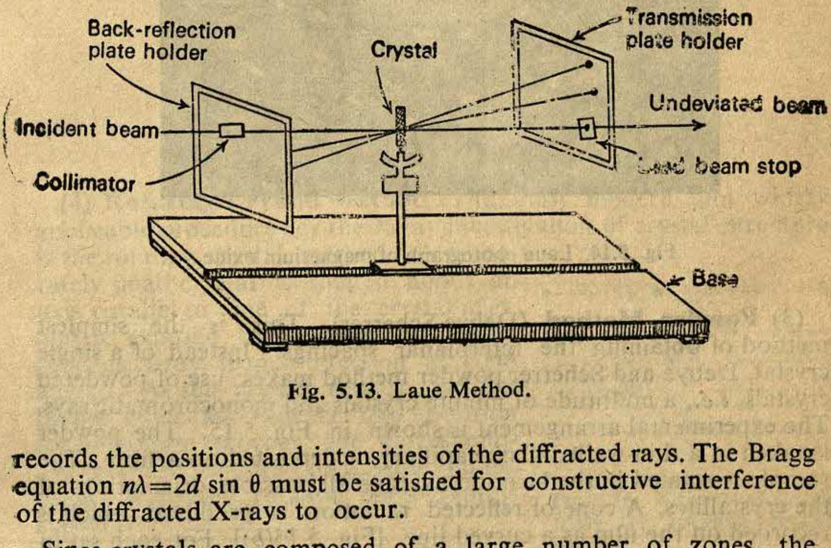


Fig. 5.13. Laue Method.

Since crystals are composed of a large number of zones, the diffraction pattern is made up of spots lying on several intersecting ellipses of hyperbolae. Some of the spots are much darker than their neighbours. These strong spots are almost invariably high-order reflections of planes of low indices. The fundamental property of Laue photographs (*see* Fig. 5.14) is that the symmetry of atomic arrangements within a crystal is largely retained in the arrangements of spots on the photographic plate.

The property of symmetry retention makes the Laue method extremely useful in problems concerning grain orientations. Laue method is not very suitable for the determination of atomic arrangements within the unit cell for finding the unknown lattice parameters. This is mainly because of the difficulty involved in identifying the wavelength corresponding to specific spot.

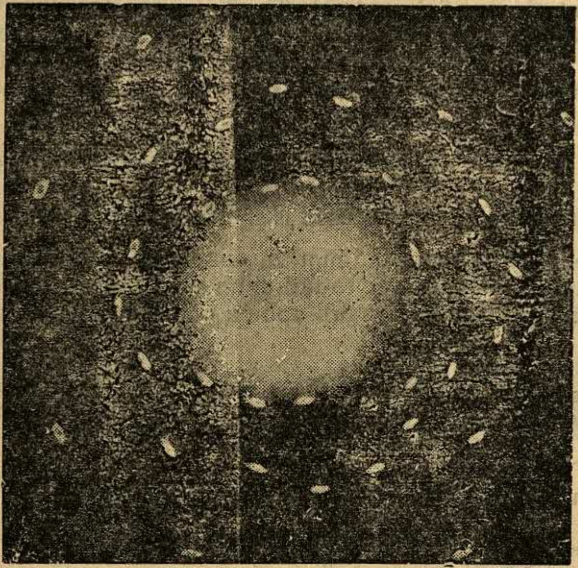
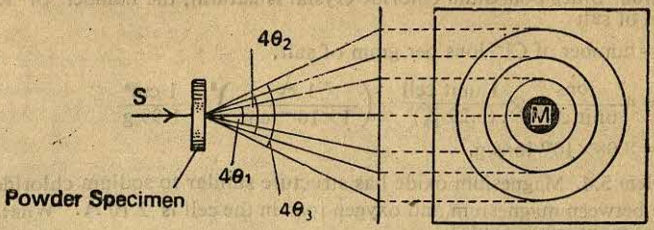


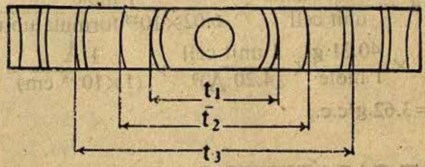
Fig. 5.14. Laue photograph of magnesium oxide.

(3) **Powder Method** (Debye-Scherrer). This is the simplest method of obtaining the interplanar spacings. Instead of a single crystal, Debye and Scherrer powder method makes use of powdered crystals, *i.e.*, a multitude of minute crystals and monochromatic rays. The experimental arrangement is shown in Fig. 5.15. The powder is taken in a thin-walled glass capillary or deposited on a fibre. The sample is rotated in the beam to average all possible orientations of the crystallites. A cone of reflected radiation is produced which is recorded on the film as a curved line. [Fig. 5.15(*b*)]. For each set of planes the reflected beam outline a cone of scattered radiation. The distances t between the lines on the film are measured accurately. From these and the diffraction angle 2θ, interplanar spacings d are calculated from the Bragg equation. In order to index the reflections, we must know the crystal system to which the specimen belongs.

The Debye-Scherrer method has the advantage of not requiring the large single crystals. A crystalline substance can be distinguished from an amorphous one since the former produces lines, the latter does not. The more precise unit cell dimensions can be calculated from high index spacings.



(a) Debye-Scherrer method



(b) A powder photograph

Fig. 5.15. X-ray diffraction by the powder method.

(4) **Rotating Crystal Method**. The most modern and widely applicable procedure for the X-ray investigation of crystal structure is the rotating crystal method. A moderately small crystal is rotated about an axis parallel to one of the crystal axes, and is exposed to a beam of homogeneous X-rays from a direction at right angles. As the crystal rotates, various planes come successively into position for diffraction to occur, and corresponding spots are produced on a photographic plate. A tepical rotation photograph is shown in Fig. 5.16.

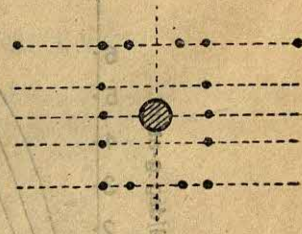


Fig. 5.16. X-ray photograph from the rotating crystal method.

Three such photographs are taken with crystal rotating about each of the three principal axes, and from the results the lattice spacing and the size of the unit cell can be deduced. If, in addition, the intensities of the various spots are measured, it is possible to determine the exact positions of the atoms or ions in the crystal. The rotating crystal method is particularly useful for complex molecules.

Problem 5.3. The potassium chloride crystal structure is like that of sodium chloride. The unit cell contains four potassium ions and four chloride ions. Given that the size of unit cell as 6.29 Å and the density of potassium chloride as 1.99 g/c.c, find the number of potassium ions and chloride ions in 1.00 g of the salt.

Solution. Since potassium chloride crystal is natural, the number of K^+ ions per gram of salt

$$= \text{number of } Cl^- \text{ ions per gram of salt.}$$

$$= 4\,\frac{\text{ions}}{\text{unit cell}} \times \frac{1 \text{ unit cell}}{(6.29\ \text{Å})^3} \times \left(\frac{1\ \text{Å}}{1 \times 10^{-8}\ \text{cm}}\right)^3 \times \frac{1\ \text{cm}^3}{1.99\ \text{g}}$$

$$= 8.08 \times 10^{21}\ \text{ions/g.}$$

Problem 5.4. Magnesium oxide has structure similar to sodium chloride. The distance between magnesium and oxygen ions in the cell is 2.10 Å. What is the density of magnesium oxide?

Solution. Length of unit cell edge $= 2 \times 2.10$ Å $= 4.20$ Å. There are four MgO formula units per unit cell.

$$\text{Density} = 4\,\frac{\text{formula units}}{\text{unit cell}} \times \frac{1 \text{ mole}}{6.02 \times 10^{23} \text{ formula units}}$$

$$\times \frac{40.31\ \text{g}}{1 \text{ mole}} \times \frac{1 \text{ unit cell}}{(4.20\ \text{Å})^3} \times \frac{1\ \text{Å}}{(1 \times 10^{-8}\ \text{cm})}$$

$$= 3.62\ \text{g/c.c.}$$

5.11. HEAT CAPACITIES OF SOLIDS

The molecules (or ions) in a solid cannot move about and normally cannot rotate; they can, however, vibrate about their mean positions.

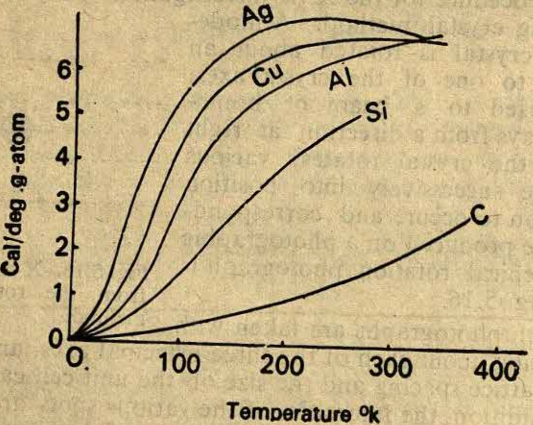


Fig. 5.17. The heat capacities of simple crystalline solids at low temperatures.

The kinetic energy in solid is therefore entirely vibrational energy. It was discovered in 1819 by Dulong and Petit that the heat capacities of solid elements, measured at ordinary temperatures, had an almost constant value of 6.3 cal/(deg) (g atom).

There are, however, exceptions to the rule. Certain elements like carbon, beryllium, boron have heat capacities less than 6.3 cal/(deg) (g atom). The essential conclusion which can be drawn from the Debye statement is that the heat capacity of an element may reach a maximum value of about 6.3 cal/(deg) (g atom) at a certain temperature called the characteristic temperature of that element. It so happens that the characteristic temperature of most elements is below room temperature, but in the case of carbon and a few other elements it is much higher.

According to the classical approach, each vibrational degree of freedom would be expected to have an average kinetic energy $\frac{1}{2}kT$ and average kinetic energy for the three perpendicular vibration modes of the atom would then be $\frac{3}{2}kT$. For a vibrating particle, as in the case of a swinging pendulum, there is constant interchange of kinetic and potential energy.

∴ For one atom

$$\begin{aligned} E &= E_{\text{kinetic}} + E_{\text{potential}} \\ &= \tfrac{3}{2}kT + \tfrac{3}{2}kT = 3kT \end{aligned}$$

and for one gram atom

$$E = 3\,NkT$$

Since the Boltzman constant $k = \dfrac{R}{N}$

$$E = 3N \times \frac{R}{N}T = 3RT$$

and $$C_p \simeq C_v = \frac{dE}{dT} = 3R \simeq 6 \text{ cal/(deg) (g. atom)}$$

Einstein has calculated the heat capacities of solids from the quantum theory. The heat capacity of a crystalline solid, containing an Avogadro's number of single particle, C_v is given by

$$C_v = 3R\left(\frac{h\nu}{kT}\right)^2 \cdot \frac{e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2} \quad \ldots (5.7)$$

where ν is the vibrational frequency.

Debye recognised that all the particles of a crystal do not vibrate with the same frequency. For small values of temperature, the Debye equation for the atomic heat capacity reduces to the form

$$C_v = 464.5\left(\frac{T}{\theta}\right)^3 \text{ cal deg}^{-1}\text{ g. atom}^{-1} \quad \ldots (5.8)$$

This equation has been found to hold at temperatures below about 25K within experimental error. The experimental values can be extrapolated to zero degrees K. It has been found that as the temperature approaches absolute zero, the heat capacity should tend toward zero. These are in agreement with the experimental observations.

PROBLEMS

1. Define and explain each of the following:

(*a*) Ionic solid

(*b*) Molecular solid

(*c*) ccp

(*d*) hcp

(*e*) Space groups.

2. What are lattice planes of a crystal? What is meant by (100), (110) and (111) planes of cubic lattices? How do the spacings of these three planes differ?

3. (*a*) Give an account of Bragg's method for the determination of the structure of crystals by means of X-rays.

(*b*) Calculate the length of edge of a single cell of a substance that crystallises in a form like NaCl. The density of the substance is 1.984 and its molecular weight is 74.56

Ans. 6.296 Å

4 Show that the volume per sphere of radius r inhibited in

(*a*) hexagonal close packing is $4\sqrt{2}\ r^3$

(*b*) face centered cubic lattice is $4\sqrt{2}\ r^3$

(*c*) Cubical packing primitive $8\ r^3$.

5. Show that the volume occupied by spheres of equal size in a close packed structure is 0.74, the value of unit cell.

6. Calculate the number of formula units in each of the following types of unit cells:

(*a*) nickel in a face-centered cubic unit cell,

(*b*) MgO in a rock salt unit cell,

(*c*) ZnS in a zinc blende unit cell.

7. The X-ray spectrum of a cubic metal of density 8.93 g ml^{-1} using radiation of $\lambda = 1.5148$ Å gave lines at the following values of θ :

21.8 25.4 37.2 45.4 47.8 58.8
68.6 72.7°

(*a*) Index the lines (*i.e.* determine the hkl values of the planes producing the lines).

(*b*) Calculate the unit cell edge length.

(*c*) Identify the type of unit cell and the element.

Ans. (*a*) 111, 200, 220, 311, 222, 400, 331, 420;
(*b*) 3.602 Å; (*c*) Face centered, Cu.

8. Calculate the spacings between (110) planes of KCl if the K^+ and Cl^- ions are taken as identical and the (100) plane spacings are 3.152 Å. Calculate the angles at which the first and second order diffraction from the (100) and the (110) planes would be observed if X-rays of wavelength 1.537 Å are used?

Ans. First order. 14°7′, for (100), 20°10′ for (110)

9. Cesium chloride forms a cubic crystal in which each Cs^+ ion is surrounded by eight Cl^- ions and likewise each Cl^- ion by eight Cs^+ ions. The density of CsCl is 3.97 g/cc. Calculate the distance between two nearest neighbour Cl ions and between Cs and Cl ions.

Ans. 4.13, 3.57 A.

10. Calculate the value of Avogadro's number from the distance between the centres of adjacent ions in NaCl, 2.82 Å and the density of NaCl (s) 2.17 gm/ml.

11. Write notes on:

(*a*) Polymorphism

(*b*) Allotropy

(*c*) Isomorphism

(*d*) Transition temperature.

12. The Na-Na distance in metallic sodium is 3.72 Å and in diatomic Na_2 it is 3.08 Å. The NaCl distance in solid NaCl is 2.814 Å, and in diatomic NaCl, it is 2.36 Å. Calculate for each case the ratio of bond length in the solid to that in the gas. The similarity is due to the fact that sodium in both the metal and in salt shares electrons with several atoms simultaneously in its vacant valence orbitals.

Ans. 121, 1.19

13. Classify each of the four following solids by type: molecular, covalent, ionic or metallic.

(*a*) rubidium chloride

(*b*) dentist's amalgam (70% Hg, 30% Cu)

(*c*) Naphthalene (moth ball) : $C_{10}H_8$

(*d*, tungsten carbide WC.

Ans. (*a*) Ionic (*b*) Metallic (*c*) Molecular (*d*) Covalent.

14. Lithium borohydride $LiBH_4$, has an orthorhombic structure with four molecules per unit cells and unit cell dimensions of $R_0=6.81$, $b_0=4.43$ and $C_0=7.17$ Å. Calculate the density of this crystal.

Ans. 0.668 gm/c.c.

15. Explain the following:

(*a*) A crystal cannot have an axis folder than six-fold of symmetry.

(*b*) LiBr, NaBr and RbBr all have the same crystal structure. However the X-ray diffraction indicates a simple cubic lattice structure for RbBr and that the other two have face centered lattices.

(*c*) Sodium chloride and potassium chloride have the same structure but different X-ray diffraction patterns.

Chapter 6

THERMODYNAMICS

6.1. INTRODUCTION

One of the most fundamental manifestations in nature is the energy changes associated with all physical and chemical transformations. There are various kinds of energy which a physical system can possess in a variety of ways such as kinetic energy, potential energy, thermal energy, chemical energy, mechanical energy, electrical energy, radiant energy, surface energy, magnetic energy, strain energy. Under certain conditions, these kinds of energy may be transformed from one form to another form. The object of thermodynamics is to seek out the relationship between kinds of energy and their diverse manifestations. The laws of thermodynamics govern the transformation of one kind of energy into another and are based on experimental facts. The term thermodynamics literally implies a field that deals with the mechanical action produced by heat.

Since thermodynamic laws deal with energy, they are applicable to all phenomena in nature. It is a science of macroscopic systems *i.e.*. systems comparatively large and involving many molecules, rather than of microscopic systems in which comparatively few molecules are involved. It requires no prior understanding of atomic and molecular structure. The basic principles of thermodynamics can be formulated without any recognition of the properties of molecules. Thermodynamics has an immense predictive power and the thermodynamic laws can be used to predict the direction in which a process would proceed. It serves as a useful guide in industrial chemistry, in space technology and nuclear engineering. Thermodynamics has certain limitations:

(1) The classical thermodynamics does not give any information at the molecular level, and this poses a serious limitation. For obtaining such an information, the laws of mechanics are first applied to molecules and then the suitable statistical averaging methods are applied to predict the behaviour of an assembly of a large number of such molecules. This constitutes the subject of *statistical mechanics*.

(2) The classical thermodynamics tells us only about the necessary conditions of chemical reactions but not the sufficient conditions. Thermodynamics does not tell us about the time required for a

reaction. In other words thermodynamics can answer the question "how far?" but, is quite unable to answer "how fast?"

6.2. THERMODYNAMIC TERMS

SYSTEM AND SURROUNDINGS

A thermodynamic system is that part of the physical universe the properties of which are under investigations. It is set off arbitrarily from the rest of the universe by a definite bounding surface. The system may be simple or complex. For example, the system may be a container of chemicals ready to react or it could be a simple vessel of a gas. The regions outside the boundaries of the system are termed as surroundings. However, the surroundings of the system are restricted to a region in the immediate vicinity of the system under study. The boundaries which separate the system from its surroundings are experimentally well defined. A system and its surroundings constitute the universe.

The ways in which interactions between a system and its surroundings take place lead to the classification of systems into the following three categories:

(*a*) **Open system**. An open system is one which can exchange both energy and matter with its surroundings.

(*b*) **Closed system**. A system is said to be closed when it can only exchange energy with its surroundings and the amount of matter in the system is not changed.

(*c*) **Isolated system**. This is a system in which there is no transfer of either energy or mass with the surroundings.

STATE OF A SYSTEM

In order to describe a thermodynamic system completely, we have to specify the values of certain measurable quantities. These are known as *thermodynamic variables* or *state variables*. A system can be completely defined by four variables namely pressure, volume, temperature and composition. The system is said to be in a certain state when all of its properties have specified values *e.g.*, if the system is homogeneous and consists of a single substance, the composition is, of course fixed, and hence the state of system depends on the pressure, volume and temperature only provided special forces such as electric or magnetic forces are absent. If these properties are fixed, all other physical properties, such as mass, density, refractive index, viscosity, dielectric constant etc., are thereby definitely fixed. The thermodynamic variables are, in general, sufficient to define a system completely.

In actual practice, all the variables need not be known because experiment has shown that three properties—pressure, volume and temperature, of a simple homogeneous system of definite mass are related to one another by the relationship called an *equation of state*.

The simplest example of such a relationship is the ideal gas equation of state, $PV=RT$. If the system is solid, liquid or heterogeneous, there is no exact quantitative relations between these three variables. Equations of state for such systems are generally considerably more complicated. The value of any one of these properties depends on the values of the other two *e.g.*, when the pressure and temperature of one mole of an ideal gas are specified, the volume must assume the value $V=\frac{RT}{P}$. Hence the thermodynamic state of a simple homogeneous system is defined by specifying any two of the three variables because the value of any one of these variables depends on the values of the other two. Thus two of the state variables are independent and one of the variables is dependent.

PROPERTIES O A SYSTEM

The physical properties of a system may be divided into two main categories:

(*i*) **Extensive properties**. These are those properties which depend upon the amount of the substance (or substances) present in the system. The examples are mass, volume, heat capacity, internal energy, entropy, Gibbs free energy, surface area etc. These properties would alter with the quantity of matter present in the system. The total value of an extensive property is equal to the sum of the values for the separate parts into which the system may, for convenience, be divided.

(*ii*) **Intensive properties**. These are those properties which are independent of the amount of substance (or substances) present in system. Examples are pressure, temperature, density, viscosity, surface tension, refractive index, electromotive force, chemical potential, specific heat etc. All these properties are characteristic of the substance (or substances) but independent of their amount.

THERMODYNAMIC EQUILIBRIUM

Thermodynamics deals only with equilibrium states in which the variables of the system have values that are uniform and constant throughout the whole system. When the observable properties of the system are not undergoing any change with time, the system is said to be in thermodynamic equilibrium. Actually this term implies three types different of equilibrium which must be attained simultaneously. These are:

(*i*) **Mechanical equilibrium.** When there is no macroscopic movements within the system itself, or of the system with respect to its surroundings, the system is in a state of mechanical equilibrium. This requires that the mechanical properties of the system must be uniform and constant. In other words, there must be no unbalanced forces acting on or within a system, since any unbalanced forces would cause the volume to change continuously and it would not be possible to specify the state of the system.

(*ii*) **Chemical equilibrium**. For a system consisting of more than one substance, if the composition does not vary with time, it is said to be in chemical equilibrium. This implies that the chemical composition of a system at equilibrium must be uniform, and there must be no net chemical reactions taking place. If some chemical change occurs, there would be change in density or temperature of the system and specification of its state would be impossible.

(*iii*) **Thermal equilibrium**. When the temperature of the system is uniform and is same as the temperature of the surroundings, it is said to be in thermal equilibrium. If there is a difference of temperature, heat will flow from higher temperature to lower temperature until the temperature difference disappears.

Consider three systems *A*, *B* and *C*. If systems *A* and *B*, and *B* and *C* are in thermal equilibrium, the systems *A* and *C* will also be in thermal equilibrium with each other which is the *Zeroth law of thermodynamics*. (Two systems which are both in thermal equilibrium with a third system are in thermal equilibrium with each other.

THERMODYNAMIC EQUILIBRIUM

When a system is displaced from equilibrium by changing its one or more variables, it undergoes a process, during which its properties change until a new equilibrium state is obtained. If a system undergoes a series of state changes in such a way that it returns to its original state, it is said to have completed a cycle and the whole process is said to be a *cyclic process*

Change of state of a system can be effected in a number of ways. When the change is carried out under such conditions that no exchange of heat is allowed between the system and surroundings, it is called an *adiabatic process*. On the other hand, if the change is carried out in such a way that the temperature throughout remains constant, it is called an *isothermal process*. If the process occurs at constant pressure, it is called an *isobaric process* while any process taking place at constant volume is known as *isochoric process*. If a process is conducted in a succession of states each of which at every instant is in a state of equilibrium, it is described as a *quasi-static process*.

6.3. MATHEMATICAL TECHNIQUES

From purely mathematical considerations, it is possible to derive a large number of equations interconnecting the state functions. Since many thermodynamic problems involve only two independent variables, the following illustrations will be limited to functions of two variables.

Equation for the total differential. Consider any thermodynamic property of a homogeneous system of constant composition which is completely determined by the three thermodynamic variables—pressure, volume and temperature. The three variables are related to each other by an equation having the functional form,

$$f(P, T, V)=0$$

Since any two of the three variables may be selected as independent, this functional relationship mny be expressed in three additional alternative forms

$$V=f(P, T), P=f(V, T), T=f(P, V)$$

Arbitrarily selecting the first one of these and utilising the principles of calculus, it is possible to write for a small increase dV in the volume V,

$$dV=\left(\frac{\partial V}{\partial P}\right)_T dP+\left(\frac{\partial V}{\partial T}\right)_P dT \qquad \ldots (6.1)$$

where the partial differential symbol, *e.g.*, $\left(\frac{\partial V}{\partial P}\right)_T$ indicates the rate of change of V with the variable P, while the other variable, T, remains constant.

Equation (6.1) can be readily utilised to find out some unknown partial derivative which cannot be readily determined experimentally. To achieve this, we make use of some transformation formulas with the help of which one can transform a partial derivative into some alternative forms. A brief illustration of some of the transformation formulas are given below:

(*i*) Suppose it is desired to determine $\left(\frac{\partial V}{\partial T}\right)_P$. Rearranging equation (6.1) to find $\frac{dV}{dT}$ and imposing the restriction that V is constant so that $dV=0$, we get

$$\frac{dV}{dT}=0=\left(\frac{\partial V}{\partial P}\right)_P \frac{dP}{dT}+\left(\frac{\partial V}{\partial T}\right)_P \qquad \ldots (6.2)$$

If it is indicated explicitly for the second factor of the 1st term on the right hand side that V is constant, and terms are rearranged, we get

$$\left(\frac{\partial V}{\partial T}\right)_P=-\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots (6.3)$$

Thus the unknown partial derivative $\left(\frac{\partial V}{\partial T}\right)_P$ can be readily converted in terms of known partial derivatives $\left(\frac{\partial V}{\partial P}\right)_T$ and $\left(\frac{\partial P}{\partial T}\right)_V$.

(*ii*) Similarly, equation (6.1) can also be rearranged by transformation formula to determine $\left(\frac{\partial V}{\partial P}\right)_T$ which is given on next page.

$$\left(\frac{\partial V}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \qquad \ldots (6.4)$$

(*iii*) Another form is obtained by rearranging equation (6.4) to

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial V}{\partial P}\right)_T \Big/ \left(\frac{\partial T}{\partial P}\right)_V \qquad \ldots (6.5)$$

and equating the right hand side of this expression to the right hand side of equation (6.3)

$$-\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial P}\right)_T \Big/ \left(\frac{\partial T}{\partial P}\right)_V$$

or

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{\left(\frac{\partial T}{\partial P}\right)_V} \qquad \ldots (6.6)$$

(*iv*) Another important relation can be derived by introducing a new but not independent variable. Consider, for example, energy, E, of a pure substance as a single valued function of pressure and temperature:

$$E = f(P, T)$$

It is possible to write

$$dE = \left(\frac{\partial E}{\partial P}\right)_T dP + \left(\frac{\partial E}{\partial T}\right)_P dT \qquad \ldots (6.7)$$

Suppose it is desired to evaluate $\left(\frac{\partial V}{\partial P}\right)_E$ in terms of other partial derivatives. Starting from equation (6.1), we find $\frac{dV}{dP}$ and then impose the restriction that E is held constant. The result obtained is the relation required.

$$\left(\frac{\partial V}{\partial P}\right)_E = \left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_E \qquad \ldots (6.8)$$

(*v*) A 5th transformation formula, for use in certain problems where a new variable G (P, T) is to be introduced, is obtained as follows:

$$\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial V}{\partial T} \cdot \frac{\partial G}{\partial G}\right)_P = \left(\frac{\partial V}{\partial G} \cdot \frac{\partial G}{\partial T}\right)_P$$

$$\left(\frac{\partial V}{\partial G}\right)_P \left(\frac{\partial G}{\partial T}\right)_P \qquad \ldots (6.9)$$

The illustrations given in this section provide the basis for many of the transformations employed in the thermodynamics of systems described by two independent variables.

6.4. STATE FUNCTIONS AND EXACT DIFFERENTIALS

Thermodynamic properties *e.g.*, energy, entropy, enthalpy, Gibbs free energy etc., are functions of state variables, and are often called *state functions.* These are independent of the path and depend only upon the initial state and final state of the system.

Consider, for example, the two quantities, $\triangle E$ (the change in internal energy) and W (work done) in moving a large boulder up a mountain, that is, against the force of gravity. The change in internal energy associated in moving from the bottom to top of the mountain is fixed whereas the work done to scale the mountain depends upon the path used. That is, the amount of work expended if a pulley is used to raise the boulder directly will be much less than the amount of work expended in bringing the boulder up the hill by pushing it over a long, rough and tortuous route. On the other hand, if the boulder is moved from the bottom to the top of mountain in many different ways, $\triangle E$ will always be the same, so long as the initial and final states of the system are the same. Thus E is a state function as its change is independent of the path whereas W is not a state function as it depends on the path.

Properties of state functions—exact differentials. The following properties are characteristics of state functions:

(*i*) Any state function *e.g.*, E, depends only on the state in which the system is, and in no way on the path along which the system got into this state. Consequently change in E of the system, $\triangle E$, when passing from state A to state B, is given by differences in values of E in the final state E_B, and original state E_A, respectively. Thus,

$$\triangle E = E_B - E_A$$

(*ii*) The differential dE is an exact differential.

(*iii*) The integral of dE about a closed path is equal to zero *i.e.*,

$$\oint dE = 0$$

The integral $\oint$ implies that the system is in the same state at the end of the path as it was at the beginning (closed path), and thus the property E is not affected by the change; dE is, therefore, an exact differential.

As an important corollary of the fact that dE is an exact differential, it can also be written as

$$dE = \left(\frac{\partial E}{\partial x}\right)_y dx + \left(\frac{\partial E}{\partial y}\right)_x dy \qquad \ldots (6.10)$$

where x and y are any other independent variables of the state of the system, for instance, any two of P, T, V.

A further useful property of exact differential expressions is the *Euler reciprocity relation.* Rewriting equation (6.10) as

$$dE = M\,dx + N\,dy$$

where M and N are defined as

$$M = \left(\frac{\partial E}{\partial x}\right)_y \qquad N = \left(\frac{\partial E}{\partial y}\right)_x$$

If dE is an exact differential, then

$$\left(\frac{\partial M}{\partial y}\right)_x=\left(\frac{\partial N}{\partial x}\right)_y \qquad \ldots (6.11)$$

This can be immediately proved as follows:

Since E is a function of state, its change must be independent of the path, and, therefore, from the principles of calculus.

$$\frac{\partial}{\partial y}\left(\frac{\partial E}{\partial x}\right)_y=\frac{\partial^2 E}{\partial y.\partial x}=\frac{\partial}{\partial x}\left(\frac{\partial E}{\partial y}\right)_x \qquad \ldots (6.12)$$

Consequently, $$\left(\frac{\partial M}{\partial y}\right)_x=\left(\frac{\partial N}{\partial x}\right)_y$$

Another test for the exactness of a differential is that it follows the cyclic rule. Thus if E is a function of x and y, *i.e.*, $E=f(x, y)$, then

$$\left(\frac{\partial E}{\partial x}\right)_y\left(\frac{\partial x}{\partial y}\right)_E\left(\frac{\partial y}{\partial E}\right)_x=-1 \qquad \ldots (6.13)$$

6.5. THE EQUIVALENCE OF HEAT AND WORK

In thermodynamics, *work (W) is defined as any quantity of energy that flows across the boundary of a system during a change in its state and is completely convertible into the lifting of a weight in the surrounding. On the other hand, heat (q) is defined as a quantity of energy that flows across the boundary of a system during a change in its state by virtue of temperature difference between the system and its surroundings and flows from a point of higher to a point of lower temperature.* These definitions imply that both work and heat are different modes of energy in transit across the boundary separating a system from its surroundings. The distinction between work and heat lies in the fact that work is energy transferred by means of a mechanical link between a system and its surroundings whereas heat is energy transferred by thermal conduction and radiation when there is a temperature difference between a system and its surroundings. To indicate the direction of transfer, we say that if work is done by the system, it is positive and if work is done on the system, it is negative. On the other hand, heat added to a system is assigned a positive symbol. and heat given by the system is assigned a negative symbol.

Work and heat are two equivalent quantities. Consider, for example, the problem of raising the temperature of a definite quantity of water, say 1 litre, by 10°C at one atmospheric pressure. This can be accomplished either by heating the water with a burner until the final state is reached, or by performing frictional work by immersing in water a stirring paddle driven by a falling weight. The amount of work could be calculated from the size of the weight and the distance through which it fell and the quantity of heat could be calculated by the temperature rise and the weight of the water. Thus the desired change of state can be accomplished by performing work alone and allowing no heat to enter or leave the system.

The above experiment is Joule's one of classic experiments on "the mechanical equivalent of heat." By using different amounts of work and various weights of water, Joule found that there was a quantitative relation between the amount of work done and the amount of heat produced. The quantitative relation between the amount of work done and the amount of heat produced is written as:

$$\ldots \quad 1 \text{ calorie} = 4.1840 \text{ Joules} = 4.1840 \times 10^7 \text{ ergs}$$

The Joule's relation is applicable to the conversion in either direction, determining the heat produced when a given amount of work is converted to heat or the work produced when a given amount of heat is converted to work although it will be seen, while discussing second law of thermodynamics that the heat cannot be completely converted into work.

The two experiments, heating the water with a burner and by stirring the water through a rotating paddle, involved the same change in state but different heat and work effects. The quantities of heat and work which flow are dependent on the path through which the process occurs. Heat and work are called *path functions*.

6.6. ENERGY AND THE CONSERVATION OF ENERGY (THE FIRST LAW OF THERMODYNAMICS)

It follows from Joule's experiments that heat and work are different forms of energy and that the form of energy can be changed but its total amount is constant *i.e.*, that energy is conserved. In other words, energy can be transferred but never created or destroyed. This is known as *the law of conservation of energy*. This law can be stated in various forms but its fundamental implication is that although energy may be converted from one form to another, it can never be created nor destroyed; in other words, whenever a quantity of one kind of energy is produced, an exactly equivalent amount of another kind (or kinds) must be used up.

The law of conservation of energy which is asserted by the first law of thermodynamics is purely the result of universal experience, for example, the failure to construct a perpetual motion machine and the constancy of the mechanical equivalent of heat. The first law of thermodynamics can be said to be universally valid for all processes as long as it is impossible to construct a perpetual motion machine and the constancy of the mechanical equivalent holds. First law is also supported by the fact that it leads to a wide variety of conclusions which are in complete conformity with the actual experience.

6.7. INTERNAL ENERGY (E)

Of the various forms of energy such as electrical, mechanical, chemical, thermal, there is another form of energy called *internal energy* or *intrinsic energy* or *energy content*. It is the energy associated with a system by virtue of its molecular constitution and the motion of its molecules. The kinetic energy of motion of individual molecule, the potential energy due to interaction between molecules, and the kinetic and potential energy of the electrons and nuclei within individual molecules all contribute to the internal energy of a substance. Change in the internal energy of a thermodynamic system is always due to change in one or more of these contributing factors. Internal energy is an extensive property and is a single valued function of the thermodynamic variables of the system. The change in internal energy of a system, associated with the passage from one thermodynamic state to another, depends only on the initial and final states, and is independent of the path followed.

6.8. WORK, HEAT AND ENERGY CHANGES

The law of conservation of energyin chemical systems can be handled in terms of three quantities, the work W that is performed, the heat q that transfers and the energy $\triangle E$ that is stored in the system. In terms of these three quantities, the first law of thermodynamics is given by the equation, $\triangle E = q - W$ which means that the difference between the heat absarbed by a system and the total work done by the system is equal to the increase in the internal energy of the system.

Let us consider a process which takes the system from state A to a higher energy state B by path 1 as shown in Fig. 6.1.

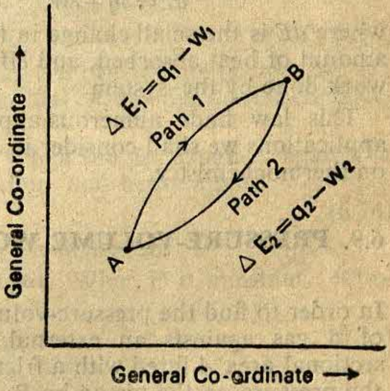


Fig. 6.1. Change of internal energy.

The system may be a container holding one or several chemical compounds. If q_1 is the amount of heat given to the system and the work done by the system be W_1 the energy changes in the process using the first law will be given by the following expression:

$$\triangle E_1 = E_B - E_A = q_1 - W_1 \qquad \ldots (6.14)$$

The relation (6.14) states that any net energy in the form of heat and work, $q_1 - W_1$, is neither created nor destroyed but is stored as $\triangle E_1$. Let the system now return from state B to state A along a different path 2 as shown in Fig. 6.1. Applying the first law of thermodynamics, we have:

$$\triangle E_2 = E_A - E_B = q_2 - W_2 \qquad \ldots (6.15)$$

The change in energy in the cyclic process $\triangle E_{A \rightarrow A}$ *i.e.*, from state

A to state *B* and back to state *A* is given by the sum of equations (6.14) and (6.15) *i.e.*,

$$\Delta E_{A\rightarrow A}=\Delta E_1+\Delta E_2 \qquad \ldots (6.16)$$

Let us assume that $\Delta E_2>\Delta E_1$. This means that energy must have been created in going around the cycle by two different paths. This is in contradiction to the first law of thermodynamics, hence

$$\Delta E_2=-\Delta E.$$

Equation (6.16) gives us

$$\Delta E_{A\rightarrow A}=\Delta E_1-\Delta E_1=0 \qquad \ldots (6.17)$$

Thus we see that the internal energy is a function of state *i.e.*, it depends only on the initial and the final state of the system and is independent of the path taken. For a cyclic process we may state:

$$\oint dE=0 \qquad \ldots (6.18)$$

For an infinitesimal process, the small change dE is an exact integral. It can easily be shown that q and W are dependent on the path the process occur and are, therefore, inexact differentials indicated as δq and δW. For an infinitesimal change, the first law is written as

$$dE=\delta q-\delta W \qquad \ldots (6.19)$$

where dE is the small change in the internal energy, δq is the small amount of heat absorbed, and δW is the small amount of external work done by the system.

This law finds numerous applications in chemistry. Some of the applications we shall consider in this chapter and in the next chapter on thermochemistry.

6.9. PRESSURE-VOLUME WORK

In order to find the pressure-volume work involved in the expansion of a gas againsts an external force, consider a cylinder of cross-sectional area *A* fitted with a frictionless and weightless piston. Let the pressure on the piston be *P*.

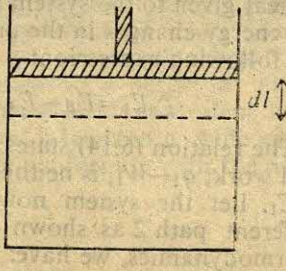


Fig. 6.2. Pressure-volume work.

Since pressure is force per unit area, the total force acting on the piston is $f=PA$. Suppose as a result of expansion, the piston moves through a distance dl. Small amount of work done, dW, by the gas on the surroundings is given by

$$dW=f.dl=PA.dl$$

But $A.dl=dV$, the increase in volume due to movement of the piston.

Therefore, $dW=PdV \qquad \ldots (6.20)$

The total work in the expansion of the gas from initial volume V_1 to the final volume V_2 is then obtained by integrating equation (6.20) between the limits V_1 and V_2, *i.e.*,

$$W=\int_{V_1}^{V_2} PdV \qquad \ldots (6.21)$$

If this is the only type of work done by the system, then substitution of equation (6.21) in the first law expression gives

$$\triangle E=q-\int_{V_1}^{V_2} PdV \qquad \ldots (6.22)$$

Equations (6.21) and (6.22) are perfectly ganeral and can be utilised to calculate W, q and $\triangle E$ in any expression or compression of the system.

We shall now discuss the special cases arising out of equations (6.21) and (6.22).

(*i*) **Constant volume.** When there is no change in volume, $dV=0$, $W=0$ and equation (6.22) takes the form

$$\triangle E=(q)_V \qquad \ldots (6.23)$$

i.e., any thermal change occurring in the calorimeter at constant volume must be the change in the internal energy due to the chemical reaction or physical transformation.

(*ii*) **Opposing pressure zero.** When the gas expands against a zero external pressure, no work is done and hence again

$$\triangle E=q \qquad \ldots (6.24)$$

This type of expansion is called *free expansion.*

(*iii*) **Opposing pressure constant.** When P is constant, equation (6.21) becomes

$$W=P(V_2-V_1) \qquad \ldots (6.25)$$

and equation (6.22) becomes

$$\triangle E=q-P(V_2-V_1) \qquad \ldots (6.26)$$

(*iv*) **Opposing pressure variable.** If P is variable it must be known as a function of volume so that equation (6.21) can be integrated. If no analytic function is available, the integration is carried out graphically by plotting P versus V and determining the area under the curve. Once W is thus known, it can be substituted into equation (6.22) to determine either $\triangle E$ or q, as the case may be.

In all calculations of W involving gas expansions, it must be kept in mind that when a volume change occurs, the amount of work done by the gas on the surroundings depends on the pressure that the surroundings exert on the system, rather than the pressure within the system itself. Further, keeping in mind that P in equation (6.21) is always a positive quantity, W will be positive if $V_2>V_1$. A positive value of W means that work is done by the gas on its surroundings. This is what happens when a system expands, pushing back its surroundings. On the other hand, if $V_2 < V_1$, then we have a compression, W is negative and work is done by the surroundings on the gas. To summarise, it can be said that in any expansion, the system does work; in a compression, work is done on the system.

6.10. REVERSIBILITY AND MAXIMUM WORK

In the study of thermodynamics we deal with the changes that occur in the properties of the system when it goes from one state to another. It is necessary to define and discuss several terms which are related to the way in which a process is carried out. A process is said to be reversible when the properties of the system at every instant remain uniform during the process. In other words in a reversible process, the change from one equilibrium state to another occurs in infinitesimal steps so that the properties of each step vary infinitesimally from those of the next step. The reversible process is an extremely slow process and would require an infinite time for its accomplishment. A reversible process is often described as a succession of states each of which is in a state of equilibrium, or as a "quasi-static process".

If the change is produced rapidly and the system does not have a chance to achieve equilibrium, the process is said to be irreversible.

Reversible processes are not real processes but are ideal ones. Real processes are always irreversible.

This concept of a reversible process is extremely useful and may be compared with the other concepts such as ideal gases, weightless strings and weightless pulleys in mechanics. *Reversible processes are of great importance because they yield maximum amount of work which may be obtained from a given net change.*

6.11. HEAT CONTENT (ENTHALPY)

Most of the chemical processes are performed at constant pressure. In order to deal with the processes at constant pressure, we define a new thermodynamic function denoted by H and is called the enthalpy or the heat content of the system. Mathematically

$$H = E + PV \qquad \ldots (6.27)$$

Since E, P and V are all functions of state, therefore, H is also a function of state. For a change in enthalpy, ΔH, we have,

$$\Delta H = \Delta E + \Delta(PV) \qquad \ldots (6.28)$$

or

$$\Delta H = \Delta E + P\Delta V + V\Delta P \qquad \ldots (6.29)$$

Since the pressure is kept constant, $\Delta P = 0$

$$\therefore \quad \Delta H = \Delta E + P\Delta V \qquad \ldots (6.30)$$

or

$$\Delta H = q_p \qquad \ldots (6.31)$$

Hence the change in enthalpy of a system is equal to the heat given to the system at constant pressure.

The importance of this new state function will become apparent when we study thermochemistry.

6.12. HEAT CAPACITIES AT CONSTANT VOLUME AND CONSTANT PRESSURE

The heat capacity of a system is defined as the heat required to raise the temperature of the system by one degree. If δq is a small quantity of heat added to the system, the temperature of the system will rise say by dT. The heat capacity C of the system is then given by

$$C=\frac{\delta q}{dT} \qquad \ldots (6.32)$$

In case of gases, we have two types of heat capacities, at constant volume and at constant pressure.

The heat capacity at constant volume, C_v can be defined as

$$C_v=\frac{\delta q_v}{dT} \qquad \ldots (6.33)$$

From the first law we have

$$q=\triangle E+P\triangle V$$

At constant volume, since $\triangle V=O$, we have

$$q_v=\triangle E \qquad \ldots (6.34)$$

∴ Heat capacity at constant volume is given by

$$C_v=\left(\frac{\partial E}{\partial T}\right)_V \qquad \ldots (6.35)$$

This equation is the thermodynamic relation defining C_v and tells us that C_v is the rate of change of internal energy with temperature at constant volume.

Further when the pressure is held constant, equation (6.32) takes the form,

$$C_v=\frac{\partial q_v}{\partial T}=\left(\frac{\partial E}{\partial T}\right)_P+P\left(\frac{\partial V}{\partial T}\right)_P$$

But if equation, $H=E+PV$, be differentiated with respect to T at constant pressure, we get

$$\left(\frac{\partial E}{\partial T}\right)_P=\left(\frac{\partial E}{\partial T}\right)_P+P\left(\frac{\partial V}{\partial T}\right)_P$$

Consequently $\quad C_p=\left(\frac{\partial H}{\partial T}\right)_P \qquad \ldots (6.36)$

Hence the heat capacity at constant pressure is defined at the rate of change of enthalpy with temperature at constant pressure.

6.13. HEAT CAPACITY RELATIONSHIPS

Since $\quad C_v=\left(\frac{\partial E}{\partial T}\right)_V$ and $C_p=\left(\frac{\partial H}{\partial T}\right)_P$

The difference between the two specific heats is given by

$$C_p-C_v=\left(\frac{\partial H}{\partial T}\right)_P-\left(\frac{\partial E}{\partial T}\right)_V \qquad \ldots (6.37)$$

But $H=E+PV$. Differentiating this quantity with respect to temperature at constant pressure we obtain,

$$\left(\frac{\partial H}{\partial T}\right)_P=\left(\frac{\partial E}{\partial T}\right)_P+P\left(\frac{\partial V}{\partial T}\right)_P$$

Substituting this into equation (6.37) we get,

$$C_p-C_v=\left(\frac{\partial E}{\partial T}\right)_P+P\left(\frac{\partial V}{\partial T}\right)_P-\left(\frac{\partial E}{\partial T}\right)_V \quad \ldots (6.38)$$

In order to relate the first and the third terms on the right of equation (6.38), we proceed as follows:

The internal energy E is a function of T and V, *i.e.*,

$$E=f(T, V)$$

and

$$dE=\left(\frac{\partial E}{\partial T}\right)_V dT+\left(\frac{\partial E}{\partial V}\right)_T dV \quad \ldots (6.39)$$

Dividing both sides of equation (6.39) by dT at constant pressure we get,

$$\left(\frac{\partial E}{\partial T}\right)_P=\left(\frac{\partial E}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P+\left(\frac{\partial E}{\partial T}\right)_V \quad \ldots (6.40)$$

On substituting equation (6.40) in equation (6.38) and cancelling $\left(\frac{\partial E}{\partial T}\right)_V$, we get

$$C_p-C_v=\left(\frac{\partial E}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P+P\left(\frac{\partial V}{\partial T}\right)_P$$

or

$$C_p-C_v=\left[\left(\frac{\partial E}{\partial V}\right)_P+P\right]\left(\frac{\partial V}{\partial T}\right)_P \quad \ldots (6.41)$$

In this equation, $P\left(\frac{\partial V}{\partial T}\right)_P$ is the work done PdV per unit increase in temperature in the constant pressure process. The other term, $\left(\frac{\partial E}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$ is the contribution from the energy required for the change in volume to pull the molecules farther apart against the cohesive or repulsive intermolecular forces. The term $\left(\frac{\partial E}{\partial V}\right)_T$ is called the internal pressure. In the case of liquids and solids, this term is significant, but in the case of gases, this term is usually small compared to P.

For ideal gases, we shall see (section 6.14) that

$\left(\frac{\partial E}{\partial V}\right)_T=0$. Hence equation (6.41) becomes

$$C_p-C_v=P\left(\frac{\partial V}{\partial T}\right)_P.$$

Further, for one mole of an ideal gas $PV=RT$, and $P\left(\frac{\partial V}{\partial T}\right)_P=R$

Hence $$C_p-C_v=R \qquad \ldots (6.42)$$

In words, the heat capacities at constant pressure and constant volume differ from each other by a constant amount, equal to the molar gas constant, *i.e.*, 1.987 cal deg^{-1} mole^{-1}.

For real gases, $C_p-C_v \approx R$

Instead of considering $E=f(T, V)$, if we consider $H=f(T, P)$, it is possible to derive another very useful relationship namely

$$C_p-C_v=\left[V-\left(\frac{\partial H}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots (6.43)$$

A third relationship between C_p and C_v may be obtained by several operations on the second term within the bracket in equation (6.43) as given below:

Since $H=f(P, T)$, we have

$$dH=\left(\frac{\partial H}{\partial T}\right)_P dT+\left(\frac{\partial H}{\partial P}\right)_T dP$$

If H is held constant during the change (called iso-enthalpic change) *i.e.*, $dH=0$, then

$$\left(\frac{\partial H}{\partial P}\right)_T dP=-\left(\frac{\partial H}{\partial T}\right)_P dT$$

or $$\left(\frac{\partial H}{\partial T}\right)_T=-\left(\frac{\partial H}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_H$$

Substituting this result into equation (6.43), we get

$$C_p-C_v=\left[V+\left(\frac{\partial H}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_H\right]\left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots (6.43a)$$

It will be seen later on that for an iso-enthalpic process,

$$\left(\frac{\partial T}{\partial P}\right)_H=\mu_{JT} \text{ (Joule-Thomson Co-efficient)}$$

and, further, since $\left(\frac{\partial H}{\partial T}\right)_P=C_p$

Hence $$C_p-C_v=\left[V+\mu_{JT}\, C_p\right]\left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots (6.43b)$$

Several other general relations between C_p and C_v can be obtained by procedures similar to those just obtained.

6.14. THE INTERNAL ENERGY OF AN IDEAL GAS (THE JOULE EXPRIMENT)

In the experiment made by Joule in 1843, it was observed that when an ideal gas was allowed to expand into a vacuum, there was n gain or loss of heat. In Joule experiment, two similar copper bulbs, one containing air under pressure and the other evacuated were connected by a wide tube with a stopcock at the middle. The surrounding water bath was stirred and its temperature recorded. When thermal equilibrium was established, the stopcock connecting the two bulbs was then opened and the temperature was again recorded. In these experiments, Joule observed no temperature change of water in the bath.

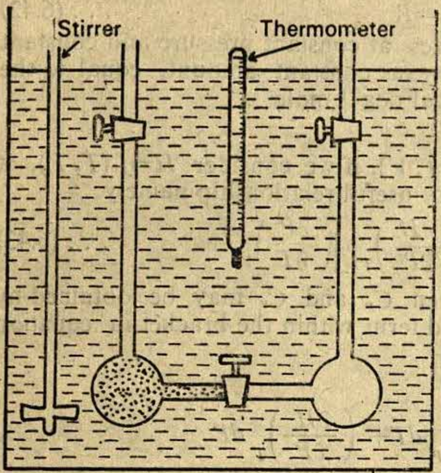


Fig. 6.3 The Joule Experiment.

From Joule's experiment, it is deduced that since the gas expands into vacuum *i.e.*, when the external pressure is zero, no work is done by the gas in its expansion. $W=0$. Further, since no heat is detected to be given up or absorbed, $q=0$. It follows, therefore, from equation, $q=\triangle E+W$, that $\triangle E$ must be zero in the process; in other words *there is no change in the internal energy of an ideal gas as a result of free expansion.* The total differential for E (which is a function of V and T) can thus be set equal to zero to give

$$dE=\left(\frac{\partial E}{\partial V}\right)_T dV+\left(\frac{\partial E}{\partial T}\right)_V dT=0$$

or on rearranging and indicating that changes in V and T are such that constant energy is maintained, we get

$$\left(\frac{\partial E}{\partial V}\right)_T=-\left(\frac{\partial E}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_E$$

Since in Joule's experiment it was observed that $\left(\frac{\partial T}{\partial V}\right)_E=0$, the above equation becomes

$$\left(\frac{\partial E}{\partial V}\right)_T=0 \qquad \text{. . . (6.44)}$$

i.e., the internal energy is independent of volume at constant temperature. This means that the energy of the gas is a function of temperature only. The result expressed by equation (6.44) is taken as one of the most important criteria of an ideal gas and is valid only for ideal gases in which the intermolecular forces of attraction are zero. For real gases, $\left(\frac{\partial E}{\partial V}\right)_T$ is a small but positive quantity.

6.15. EFFECT OF PRESSURE AND TEMPERATURE ON HEAT CAPACITIES OF IDEAL GASES

As discussed above, since the internal energy of an ideal gas is independent of volume at constant temperature, it should also be independent of pressure. The energy of a given quantity of gas only varies with temperature. Thus for an ideal gas, it is possible to write down equation for C_v as

$$C_v=\frac{dE}{dT} \qquad \ldots (6.45)$$

This indicates that heat capacity at constant volume of an ideal gas is independent of the volume or the pressure of the gas.

Similarly, it can also be shown that for an ideal gas, *H is a function of temperature only and heat capacity at constant pressure is also a function of temperature only.*

This can be easily proved as given below:

We have $H=E+PV$.

Differentiating this equation with respect to volume at constant temperature, we get

$$\left(\frac{\partial H}{\partial V}\right)_T=\left(\frac{\partial E}{\partial V}\right)_T+\left[\frac{\partial (PV)}{\partial V}\right]_T$$

Again, for an ideal gas, $\left(\frac{\partial E}{\partial V}\right)_T=0$ and $\left[\frac{\partial (PV)}{\partial V}\right]_T$ is also zero, since $PV=RT$, so that $\left(\frac{\partial H}{\partial V}\right)_T=0$.

Thus for an ideal gas, we have

$$C_p=\frac{dH}{dT} \qquad \ldots (6.46)$$

Equations (6.45) and (6.46) are always valid for an ideal gas regardless of what kind of process is considered. Implicit in these statements is the fact that for an ideal gas, E and C_v as well as H and C_p are functions of temperature only, independent of volume and pressure.

6.16. HEAT CAPACITY—TEMPERATURE RELATIONSHIPS

Both C_p and C_v for all gases increase with temperature. Some empirical expressions which represent this variation have been predicted from experimental measurements. One of the commonly used relation is a power series of the form

$$C_p=\alpha+\beta T+\gamma T^2+\delta T^3+\ldots \qquad \ldots (6.47)$$

where α, β, γ, δ etc. . . are constants and can be determined from the experimentally determined heat capacities over a range of temperature, temperature being expressed in absolute degrees.

The mean heat capacity, $\overline{C_p}$, over a range temperature, say from T_1 to T_2, is given by

$$\overline{C_p} = \frac{\int_{T_1}^{T_2} C_p \, Tp}{T_2 - T_1} \qquad \ldots (6.48)$$

Substituting the value of C_p from equation (6.47) into equation (6.48) and integrating, we get

$$\overline{C_p} = \frac{1}{T_2 - T_1}\left[\alpha(T_2 - T_1) + \tfrac{1}{2}\beta(T_2^2 - T_1^2) + \tfrac{1}{3}\gamma(T_2^3 - T_1^3) + \ldots\right]$$

$$= \alpha + \tfrac{1}{2}\beta(T_2 + T_1) + \tfrac{1}{3}\gamma(T_2^2 + T_1 T_2 + T_1^2) + \ldots \qquad \ldots (6.49)$$

Knowing the constants, it is possible to determine $\overline{C_p}$ for any gas over any temperature change.

The amount of heat required to raise the temperature of a gas from T_1 to T_2 at constant pressure is obtained by integrating the equation, $dH = C_p \, dT$, using equation (6.47) to express C_p as a function of temperature *i.e.*,

$$\int_{H_1}^{H_2} dH = \int_{T_1}^{T_2} C_p \, dT = \int_{T_1}^{T_2} (\alpha + \beta T + \gamma T^2 + \delta T^3 + \ldots)\, dT$$

$$\text{or } H_2 - H_1 = \alpha(T_2 - T_1) + \tfrac{1}{2}\beta(T_2^2 - T_1^2) + \gamma(T_2^3 - T_1^3) + \ldots \qquad \ldots (6.50)$$

6.17. ISOTHERMAL PROCESS

In an isothermal process, the temperature is maintained constant during the entire operation. Since the internal energy of an ideal gas varies with temperature only, imposition of constant temperature implies constancy of E *i.e.*, for an isothermal process, $\triangle E = 0$ and hence the equation $\triangle E = q - W$ reduces to $q = W$.

But, as discussed in section 6.9, the total work obtained in the expansion of a gas from initial volume V_1 to the final volume V_2 is equal to the integral of the pressure times the differential of the volumef *i e.*,

$$q = W = \int_{V_1}^{V_2} P dV$$

Thus, in an isothermal process, all the work performed is obtained at the expense of absorbed heat and *vice-versa*. The magnitude of q will thus vary with W and may range from zero for a free expansion to a maximum for reversible process.

The expression for the maximum work in an isothermal reversible expansion of an ideal gas is obtained as follows:

Since
$$W_{max}=\int_{V_1}^{V_2} PdV \qquad \ldots (6.51)$$

For an ideal gas, $PV=nRT$ and the pressure is given by $P=\frac{nRT}{V}$. Substituting this in equation (6.51), we have

$$W_{max}=\int_{V_1}^{V_2}\frac{nRT}{V}dV$$

$$=nRT\int_{V_1}^{V_2}\frac{dV}{V}$$

$$=nRT\ln\frac{V_2}{V_1}$$

or
$$W_{max}=2.303\ nRT\ \log\frac{V_2}{V_1}. \qquad \ldots (6.52)$$

Equation (6.52) gives the maximum amount of work obtainable in the isothermal reversible expansion of n moles of an ideal gas from volume V_1 to V_2 at constant temperature T. Again since the temperature is constant, $\frac{V_2}{V_1}=\frac{P_1}{P_2}$.

Therefore, equation (6.52) can also be written as

$$W_{max}=nRT\ln\frac{P_1}{P_2}$$

or
$$W_{max}=2.303\ nRT\ \log\frac{P_1}{P_2} \qquad \ldots (6.53)$$

For real gases, $\triangle E\neq 0$ under isothermal conditions because, even when temperature is constant, internal energy will change due to change in volume or pressure. The same is true for $\triangle H$.

Problem 6.1. Calculate the maximum work obtainable by the isothermal reversible expansion of 2 moles of nitrogen from 10 litres to 20 litres at 25°C.

Solution. Since $W_{max}=nRT\ln\frac{V_2}{V_1}$

$$=2.303\ nRT\ \log\frac{V_2}{V_1}$$

Here $n=2$ moles, $V_2=10$ litres, $V_1=10$ litres

$R=1.987$ cal deg^{-1} mole^{-1} and $T=273.2+25=298.2$ K

$$\therefore \quad W_{max}=2.303\times 2\times 1.987\times 298.2\times\log\frac{20}{10}$$

$$=822\ \text{c}\ :$$

Problem 6.2. If one mole of ice at 0°C and 4.6 mm Hg pressure is converted to water vapor at the same temperature and pressure by increasing the space above ice sufficiently, calculate the enthalpy and intrinsic energy change. Latent heat of fusion of ice is 80 calories per g. and latent heat of vaporisation of liquid water at 0°C is 596 calories per gram.

Solution.

$$\triangle E = q_p - P\triangle V$$

$$\triangle H = \triangle E + P\triangle V = q_p$$

Heat absorbed when one gram mole of ice in being converted to one mole of water at 0°C and 4.6 mm Hg pressure

$$= 80 \times 18 = 1440 \text{ calories}$$

Heat absorbed by one mole of water in being converted to one mole of water vapour

$$= 596 \times 18 = 10728 \text{ calories.}$$

For the total change, $q_p = 1440 + 10728$

$$= 12168 \text{ calories.}$$

Volume of one mole of water vapor at 0°C and 4.6 mm Hg pressure (through gas equation) $= 22.4 \times \frac{760}{4.6}$

$$= 3717 \text{ litres.}$$

Ignoring the volume of ice in comparison with the volume of water vapor

$$\triangle V = 3717 \text{ litres}$$

$$P\triangle V = 3717 \times \frac{4.6}{760} = 22.4 \text{ litre-atmosphere}$$

$$= \frac{22.4 \times 10^8 \times 76 \times 13.6 \times 980}{4.18 \times 10^7}$$

$$= 543 \text{ calories.}$$

$$\triangle E = 12168 - 543 = 11625 \text{ calories}$$

$$\triangle H = 11625 + 543 = 12168 \text{ calories.}$$

Problem 6.3. An ideal gas undergoes a reversible isothermal expansion from an initial volume V_1 to a final volume $10\,V_1$ and thereby does 10,000 cal of work. The initial pressure was 100 atm. (*a*) Calculate V_1. (*b*) If there were 2 moles of gas, what must its temperature have been?

Solution. (*a*) Since $W = 2{,}303\ nRT \log \frac{V_2}{V_1} = 2.303\ nRT \log \frac{10V_1}{V_1}$

$$= 2.303\ nRT$$

But $P_1V_1 = nRT = \frac{W}{2.303}$

$$100 \times V_1 = \frac{10{,}000}{2.303}$$

$\therefore$ $V_1 = \frac{10{,}000}{2.303} \times \frac{1}{100} \times (0.041 \text{ litre atm/cal})$

or $V_1 = 1.78$ litres.

(*b*) If $n = 2$

$$W = 2.303\ nRT \log \frac{10V_2}{V_1}$$

$$W = 2.303\ nRT$$

$$nRT = \frac{W}{2.303}$$

$$RT=\frac{10,000}{2.303\times 2}$$

or
$$T=\frac{10,000}{2.303\times 2\times 1.98}$$

$$T=1100\text{K}.$$

6.18. ADIABATIC PROCESSES

An adiabatic process is one in which there is no exchange of heat between the system and its surroundings. In other words, in an adiabatic process no heat enters or leaves the system, so that $q=0$ and work is done at the expense of the internal energy of the gas. Thus if work is done on the system, the internal energy of the system will increase. Conversely if work is done by the system, the internal energy of the system decreases and consequently the temperature of the system drops. Let us consider 1 mole of an ideal gas. Since for an adiabatic process, $q=0$, from the first law we have

$$dE=-W=-PdV$$

From equation (6.45), we have $dE=C_vdT$. Substituting this in the above equation, we get

$$C_vdT=-PdV \qquad \ldots (6.54)$$

For an ideal gas, $P=\frac{RT}{V}$. Substituting the value of P and on rearranging, we have

$$C_v\frac{dT}{T}=-R\frac{dV}{V} \qquad \ldots (6.55)$$

Here C_v is assumed to be independent of temperature. For a process that takes the gas from a volume V_1 at a temperature T_1 to a new volume V_2 and temperature T_2, we have

$$C_v\int_{T_1}^{T_2}\frac{dT}{T}=-R\int_{T_1}^{V_2}\frac{dV}{V}$$

or
$$\frac{C_v}{R}\ ln\ \frac{T_2}{T_1}=-\ ln\ \frac{V_2}{V_1} \qquad \ldots (6.56)$$

On rearranging equation (6.56), we have

$$ln\ \frac{T_2}{T_1}=ln\ \left(\frac{V_1}{V_2}\right)^{R/C_v} \qquad \ldots (6.57)$$

Further, for an ideal gas, we have the relation between C_p and C_v as

$$C_p-C_v=R$$

Substituting this in equation (6.57), we get

$$ln\,\frac{T_2}{T_1}=ln\,\left(\frac{V_1}{V_2}\right)^{\frac{C_p-C_v}{C_v}}$$

or
$$ln\,\frac{T_2}{T_1}=ln\,\left(\frac{V_1}{V_2}\right)^{\gamma-1} \qquad \ldots (6.58)$$

where $\frac{C_p}{C_v}=\gamma$, the ratio of heat capacities at constant pressure and constant volume. Taking antilogarithm of both sides of equation (6.58), we get

$$\frac{T_2}{T_1}=\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

or
$$T_2V_2{}^{\gamma-1}=T_1V_1{}^{\gamma-1} \qquad \ldots (6.59)$$

Further, for 1 mole of an ideal gas, $PV=RT$

or
$$T=\frac{PV}{R}$$

Substituting the value of T in equation (6.59), we get

$$\frac{P_2V_2}{R}\,(V_2)^{\gamma-1}=\frac{P_1V_1}{R}\,(V_1)^{\gamma-1}$$

or
$$P_2V_2{}^{\gamma}=P_1V_1{}^{\gamma} \qquad \ldots (6.60)$$

Similarly, substituting V by $\frac{RT}{P}$ in equation (6.60), we have

$$P_2\left(\frac{RT_2}{P_2}\right)^{\gamma}=P_1\left(\frac{RT_1}{P}\right)^{\gamma}$$

or
$$T_2{}^{\gamma}\,P_2{}^{1-\gamma}=T_1{}^{\gamma}\,P_1{}^{1-\gamma} \qquad \ldots (6.61)$$

The results of equations (6.59), (6.60) and (6.61) may be summarised in the convenient form

$$TV^{\gamma-1}=\text{constant},\ PV^{\gamma}=\text{constant},$$

and
$$TP^{\frac{1-\gamma}{\gamma}}=\text{constant}.$$

These relationships will always hold in an adiabatic mechanical change of an ideal gas.

In an isothermal change, PV=constant and for an adiabatic change, PV^{γ} =constant where $\gamma>1$. If a comparison be made of the reversible work obtained from an adiabatic expansion and isothermal expansion, one can see that for the same initial pressure and volume, isothermal expansion results in a larger final pressure than the final pressure for adiabatic expansion. This is shown in Fig. 6.4. The reason for this lies in the fact that adiabatic expansion is accompanied by fall of temperature which will tend to diminish the volume. But in the isothermal process, the temperature is constant.

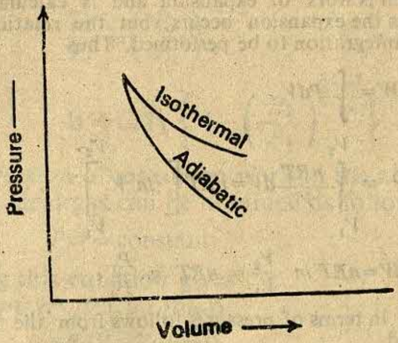


Fig. 6.4. Adiabatic and isothermal processes.

Problem. 6.4. Calculate q, W and $\triangle E$ for the conversion, at 100°C and 1 atm. of 1 mole of water into steam, for which the heat of vaporisation is 9720 cals.

Solution. The heat required for this purpose is the latent heat of vaporization, which is 9720 cal/mole. Thus we have immediately

$$q=9720 \text{ cal.}$$

Since the work done in the process results from the expansion of the system, it is calculated from $W=PdV$.

Further more, the pressure remains constant, and the integration gives

$$W=\int_{V_1}^{V_2} PdV=P\int_{V_1}^{V_2} dV$$
$$=P(V_2-V_1)$$

The volume of one mole of liquid water V_1 is about 18 c.c., and the volume of 1 mole of steam V_2 can be estimated from

$$V_2=\left(\frac{373}{273}\right)(22400)$$
$$=30600 \text{ c.c.}$$

The work of expansion is then obtained as

$$W=(1)(30600-18)=30582 \text{ c.c. atm}$$
$$=740 \text{ cal.}$$

The first law equation now allows the calculation of the internal energy change as

$$\triangle E=q-W=9720-740=8980 \text{ cal.}$$

For this process, most of the added heat is seen to go into increasing the internal energy of the water, and only a small fraction is expanded in pushing back the atmosphere.

Problem 6.5. Calculate q, W and $\triangle E$ for the reversible expansion of 10 moles of an ideal gas from an initial pressure of 1 atm to a final pressure 0.1 atm at a constant temperature of 0°C.

Solution. The internal energy of an ideal gas depends only on the temperature. In this expansion, the temperature remains constant, and we can write

$$\triangle E=0.$$

Again the work term is work of expansion and is calculated from $\int PdV$. Both P and V change as the expansion occurs, but the relation $PV=nRT$, with constant T, allows the integration to be performed. Thus

$$W=\int PdV$$

$$=\int_{V_1}^{V_2} \frac{nRT}{V}dV=nRT\Big[\ ln\ V\ \Big]_{V_1}^{V_2}$$

or $$W=nRT\ ln\ \frac{V_2}{V_1}=nRT\ ln\ \frac{P_1}{P_2}.$$

The final expression in terms of pressures follows from the fact that the temperature is constant, and

$$P_1V_1=P_2V_2$$

or $$\frac{V_2}{V_1}=\frac{P_1}{P_2}$$

Substitution of numerical values gives

$$W=(10)\ (1.987)\ (273)(2.303)\ \log\ \frac{1.0}{0.1}$$

$$=1250 \text{ cal.}$$

Finally, the first law expression is used to obtain q

$\because$ $$q=\triangle E+W$$

$$=0+1250$$

$$=1250 \text{ cal.}$$

In this example, all the absorbed heat is expanded in the work of expansion, and the internal energy of the gas remains unchanged.

6.19. WORK OF EXPANSION IN REVERSIBLE ADIABATIC PROCESS

We have

$$w=PdV$$

This equation gives the work of expansion W in an infinitesimal stage of a reversible, adiabatic process *i.e.*, PdV which is equal to $-C_vdT$ (from equation 6.54). For an appreciable process, the total work of expansion, W, is given by

$$W=\int_{V_1}^{V_2} PdV=-\int_{T_1}^{T_2} C_vdT \qquad \ldots (6.62)$$

Assuming C_v to be constant, equation (6.62) can be integrated to yield

$$W=-C_v(T_2-T_1)=C_v(T_1-T_2) \qquad \ldots (6.63)$$

or $$W=C_vT_1\left(1-\frac{T_2}{T_1}\right)$$

But, since $$\frac{T_2}{T_1}=\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

$\therefore$ $$W=C_vT_1\left\{1-\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right\} \qquad \ldots (6.64)$$

An other expression of maximum work in the adiabatic reversible expansion of an ideal gas can be obtained as follows:

$\because$ $$Pv^{\gamma}=\text{constant}$$

Differentiating this equation gives

$$\gamma PV^{\gamma-1}dV+V^{\gamma}dP=0$$

$$\gamma PdV+VdP=0$$

$$VdP=-\gamma PdV \qquad \ldots (6.65)$$

Further, from complete differential of $PV=RT$, we have

$$PdV+VdP=RdT$$

or $$VdP=RdT-PdV \qquad \ldots (6.66)$$

Substituting the value of VdP from equation (6.66) into equation (6.65), we get

$$RdT-PdV=-\gamma PdV$$

or $$PdV=\frac{RdT}{(1-\gamma)} \qquad \ldots (6.67)$$

For n moles, this equation becomes

$$PdV=\frac{nRdT}{(1-\gamma)} \qquad \ldots (6.68)$$

Further, $\because$ $$W_{max}=\int_{V_1}^{V_2} PdV$$

Substituting PdV from equation (6.67) into this equation and changing the limits to the temperatures corresponding to the volumes, we get

$$W_{max}=\int_{V_1}^{V_2} PdV=\int_{T_1}^{T_2}\frac{RdT}{(1-\gamma)}$$

or $$W_{max}=\frac{R(T_2-T_1)}{(1-\gamma)} \qquad \ldots (6.69)$$

when $T_2>T_1$, W_{max} is negative meaning that work is done on the gas. But, if $T_2<T_1$, W_{max} is positive and work is done by the gas.

TABLE 6.1

Thermodynamic changes in isothermal expansion of an ideal gas

Reversible	*Free*	*Actual*
$T_1=T_2$	$T_1=T_2$	$T_1=T_2$
$W=nRT ln\frac{V_2}{V_1}$	$W=0$	$O<W<nRT\ ln\ \frac{V_2}{V_1}$
$\triangle U=0$	$\triangle U=0$	$\triangle U=0$
$Q=nRT\ ln\frac{V_2}{V_1}$	$Q=0$	$O<Q<nRT\ ln\ \frac{V_2}{V_1}$
		$Q=W$
$\triangle H=0$	$\triangle H=0$	$\triangle H=0$

TABLE 6.2

Thermodynamic changes in adiabatic expansion of an ideal gas.

Reversible	*Free*	*Actual*
V_1	V_1	V_1
V_2	V_2	V_2
$W=-C_v\,(T_2-T_1)>0$	$W'=C_v(T_2'-T_1)=0$	$W''=-C_v(T_2''-T_1)>0;$
$\therefore\ T_2<T_1$	$\therefore\ T_2'=T_1$	$W''<W$
		$\therefore\ T_2''<T_1\,;$
		but $T_2''>T_2$
$\triangle U=C_v(T_2-T_1)<0$	$\triangle U'=0$	$\triangle U''=C_v(T_2''-T_1)<0$
$\triangle H=C_p(T_2-T_1)<0$	$\triangle H'=0$	$\triangle H''=C_p(T_2-T_1)<0$

Problem 6.6. Calculate the work of expansion of 1 mole of an ideal gas initially at 25°C, the pressure being changed from 1 to 5 atm under (*a*) Isothermal conditions and (*b*) Adiabatic conditions. (Given $C_p=7.0$ cal deg^{-1} $mole^{-1}$ and $C_v=5.0$ cal deg^{-1} $mole^{-1}$).

Solution. (*a*) Under Isothermal conditions,

$$W_{\text{isothermal}}=2.303\ RT\log\frac{P_1}{P_2}$$

Here $R=8.313\times10^7$ ergs, $T=273.2+25=298.2$ K,

$P_1=1$ atm and $P_2=5$ atm

$$\therefore\quad W_{\text{isothermal}}=2.303\times8.313\times10^7\times298.2\log\frac{1}{5}$$

$$=-3.99\times10^{10}\text{ ergs mole}^{-1}$$

(*b*) Under Adiabatic conditions,

$$W_{\text{adiabatic}}=C_vT_1\left[1-\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right]$$

$C_v=5.0\times4.187\times10^7$ ergs deg^{-1} $mole^{-1}$

Here $T_1=298.2$ K,

$$\gamma=\frac{C_p}{C_v}=\frac{7}{5}\quad\text{or}\quad\frac{\gamma-1}{\gamma}=\frac{2}{7}$$

$P_1=1$ atm and $P_2=5$ atm

$$\therefore \quad W_{\text{adiabatic}} = 5.0\times4.187\times10^{7}\times298.2\left[1-\left(\frac{5}{7}\right)^{\frac{2}{7}}\right]$$
$$= -3.64\times10^{10} \text{ ergs mole}^{-1}.$$

Problem 6.7. 2 moles of N_2 at S.T.P. are compressed reversibly to a volume of 10 litres. Calculate the work done when the process is carried out (*a*) isothermally and (*b*) adiabatically. (Given $\gamma=1.40$).

Solution. (*a*) Under isothermal conditions

$$W_{\text{isothermal}} = 2.303\ RT \log \frac{V_2}{V_1}$$

Here $V_1=2\times22.4=44.8$ litres, $V_2=10$ litres.

$R=8.313\times10^{7}$ and $T=273.2$ K

$$\therefore \quad W_{\text{isothermal}} = 2.303\times8.313\times10^{7}\times273.2 \log \frac{10}{44.8}$$
$$= -3{,}405\times10^{10} \text{ ergs deg}^{-1} \text{ mole}^{-1}.$$

(*b*) Under adiabatic conditions,

$$W_{\text{adiabatic}} = \frac{R(T_2-T_1)}{1-\gamma}$$

Here, $T_1=273.2$, $R=8.313\times10^{7}$, $\gamma=1.40$ and $T_2=?$

T_2 can be obtained as follows:

$$\because \quad T_2V_2^{\gamma-1}=T_1V_1^{\gamma-1}$$

or $T_2\times(10)^{1.40-1}=273.2\times(44.8)^{1.40-1}$

or $T_2=497.4$ K.

$$\therefore \quad W_{\text{adiabatic}} = \frac{8.313\times10^{7}(497.4-273.2)}{1-1.40}$$
$$= -4.663\times10^{11} \text{ ergs deg}^{-1} \text{ mole}^{-1}.$$

6.20. JOULE-THOMSON EFFECT

Joule-Thomson porous plug experiment is one of the very important methods for the quantitative measurement of deviations from ideal behaviour of a thermodynamic system from the determinations of the change in temperature.

Their apparatus is shown in Fig. 6.5.

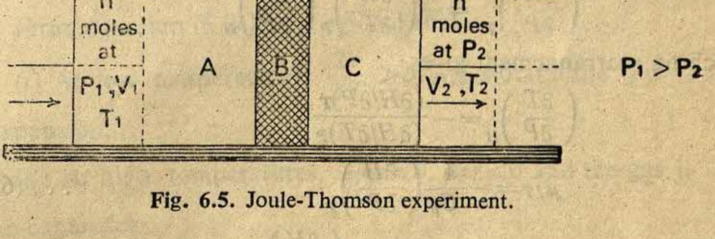


Fig. 6.5. Joule-Thomson experiment.

A gas from a high pressure region *A* is allowed to pass to a low pressure region *C* through a throttle *B* which consists of a porous plug. The gas emerging at *C* attains an equilibrium and its temperature can be measured directly. The entire system is thermally insulated, so that the process is an adiabatic one, and $q=0$. Let P_1 be the pressure, V_1 the volume and T_1 the temperature of the gas before it expands and P_2, V_2 and T_2 be the final pressure, volume and the temperature of the gas.

The work done on the gas before it is forced through the porous plug, will be $-P_1V_1$ and the work done by the gas in expansion will be P_2V_2 and hence the net work done by the system is $W=P_2V_2-P_1V_1$. Since the process is being carried out adiabatically, $q=0$, and therefore, applying the first law, we have

$$\triangle E=E_2-E_1=W=-(P_2-V_2-P_1V_1)$$

or
$$E_2=E_1+P_1V_1-P_2V_2$$

$$E_2+P_2V_2=E_1+P_1V_1$$

$$\therefore \qquad H_2=H_1 \qquad (\because \; H=E+PV)$$

or
$$\triangle H=0$$

In words, the heat content of a system during its expansion through a throttle remains constant.

Joule-Thomson coefficient (μ_{JT}). It is the rate of change of temperature with the pressure which is observed when the gas flows through a throttle from a higher pressure to a lower pressure.

Mathematically, Joule-Thomson coefficient (μ_{JT}) is represented as

$$\mu_{JT}=\left(\frac{\partial T}{\partial P}\right)_H \qquad \ldots (6.70)$$

Derived relations. For purpose of evaluation, it is frequently essential to express the Joule-Thomson coefficient in terms of other partial derivatives.

Since
$$H=f\,(P, T)$$

$$dH=\left(\frac{\partial H}{\partial P}\right)_T dP+\left(\frac{\partial H}{\partial T}\right)_P dT$$

Imposing the restriction of constant enthalpy, we get

$$\left(\frac{\partial H}{\partial P}\right)_T=-\left(\frac{\partial H}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_H$$

which on rearrangement gives

$$\left(\frac{\partial T}{\partial P}\right)_H=-\frac{(\partial H/\partial P)_T}{(\partial H/\partial T)_P}$$

or
$$\mu_{JT}=-\frac{1}{C_p}\left(\frac{\partial H}{\partial P}\right)_T \qquad \ldots (6.71)$$

Thus μ_{JT} can be calculated from $\left(\frac{\partial H}{\partial P}\right)_T$ or *vice versa.*

Again utilising the relationship $H=E+PV$ in equation (6.71), another relation of interest is obtained which is given below:

$$\mu_{JT}=-\frac{1}{C_p}\left[\left(\frac{\partial E}{\partial P}\right)_T+\left(\frac{\partial[PV]}{\partial P}\right)_T\right] \qquad \ldots (6.72)$$

and since E is a function of P, V and T, which are not independent, it follows:

$$\mu_{JT}=-\frac{1}{C_p}\left[\left(\frac{\partial E}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T+\left(\frac{\partial[PV]}{\partial P}\right)_T\right] \qquad \ldots (6.73)$$

Equation (6.73) is perfectly general and is applicable to any gas. Further, for an ideal gas, since $\left(\frac{\partial E}{\partial V}\right)_T=0$ and also $\left(\frac{\partial[PV]}{\partial P}\right)_T=0$, it follows from the above equation that $\mu_{JT}=0$. Thus, the Joule-Thomson coefficient for an ideal gas is zero which implies that when an ideal gas expands through a throttle, no change of temperature is observed.

Joule-Thomson experiments with real gases showed that as a gas approaches ideal behaviour, the Joule-Thomson effect becomes less marked. Since there is no attraction between the molecules of an ideal gas, no work is done by the gas on the surroundings and no heat is given up or absorbed.

Inversion temperature. A positive μ_{JT} indicates the expansion of a gas which results in cooling. On the other hand, a negative μ_{JT} refers to the warming of the gas. It has been observed that μ_{JT} is positive at and below room temperature for all gases except H_2 and He and at sufficiently high temperatures, μ_{JT} is negative for all gases. If the temperature is suitably low, even H_2 and He show a cooling effect during expansion. Thus for each gas, there is at least one temperature at which μ_{JT} changes sign, and hence is zero. For example, hydrogen is warmed if the initial temperature is above −80°C and shows cooling effect below−80°C on expansion. At this temperature, $\mu_{JT}=0$ and this temperature is called the *inversion temperature*. At inversion temperature, the gas neither heats nor cools on expansion.

It can be proved that for a gas obeying van der Waals equation

$$\mu_{JT}=\frac{1}{C_p}\left(\frac{2a}{RT}-b\right) \qquad \ldots (6.74)$$

From equation (6.74), it is evident that

(*i*) At low temperatures, $\frac{2a}{RT}>b$, $\mu_{JT}>0$ and the gas cools on expansion.

(*ii*) At high temperatures, $\frac{2a}{RT}<b$, $\mu_{JT}<0$ and the gas is heated on expansion.

(*iii*) At some intermediate temperature, $\frac{2a}{RT}=b$, $\mu_{JT}=0$ and no change in temperature is observed on expansion. Obviously, this is the inversion temperature, T_i, and we have

$$\frac{2a}{RT_i}=b$$

or

$$T_i=\frac{2a}{Rb}$$

Thus, if van der Waals constants are known, T_i can be calculated.

The Joule-Thomson effect can be used as the basis for liquefaction of gases, refrigeration and steam engineering.

PROBLEMS

1. Explain clearly the terms:
System, surroundings, state of system, change of state.

2. What do you understand by the terms internal energy and enthalpy of a system? How are they inter-related?

3. A gas expands against a variable opposing pressure given by $P=\frac{10}{V}$ atm, where V is the volume of the gas at each state of the expansion. Further, in expanding from 10 to 100 litres, the gas undergoes a change in internal energy of $\triangle E=100$ cal. How much heat is absorbed by the gas during the process?

Ans. $q=668$ cal.

4. Two litres of N_2 at 0°C and 5 atm pressure are expanded isothermally against a constant pressure of 1 atm until the pressure of the gas is also 1 atm. Assuming the gas to be ideal, what are the values of W, $\triangle E$, $\triangle H$ and q for the process?

Ans. $W=q=194$ cal ; $\triangle E=\triangle H=0$.

5. One mole of an ideal gas is allowed to expand reversibly *i.e.*, against a confining pressure that is at all times infinitesimally less than the gas pressure, from an initial pressure of 10 atm to a final pressure of 0.4 atm, the temperature being kept constant at 0°C.

(*a*) How much work is done by the gas?

(*b*) What is the change in E and H?

(*c*) How much heat is absorbed?

Ans. (*a*) $W=1910$; (*b*) $\triangle E=\triangle H=0$; $q=1910$ cal.

6. For a certain ideal gas, $C_p=8.58$ cal mole^{-1} degree^{-1}. What will be the final volume and temperature when 2 moles of the gas at 20°C and 15 atm are allowed to expand adiabatically and reversibly to 5 atm pressure?

Ans. $V=7.45$ litres; $t=46$°C

7. Show that the work done in a reversible adiabatic expansion of 1 mole of an ideal gas is given by the relation

$$W=C_vT_1\left[\ 1-\left(\frac{P_2}{P_1}\right)^{\frac{R}{C_p}}\right]$$

if C_p and C_v are independent of temperature.

8. Show that each of the relations given below simplifies to $C_p—C_v=R$ for an ideal gas

(*a*) $$C_p—C_v=\left[P+\left(\frac{\partial E}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

(*b*) $$C_p - C_v = -T\frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T}$$

(*c*) $$C_p - C_v = TV\ \frac{\alpha^2}{\beta} \text{ where } \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\text{and } \beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

9. For a van der Waals gas, the Joule-Thomson coefficient is given by

$$\mu_{JT} = \frac{1}{C_p}\left(\frac{2a}{RT} - b - \frac{3abP}{R_2T_2}\right)$$

Show that the temperature of inversion as a function of pressure is given by the relation

$$T_i = \frac{a \pm \sqrt{a^2 - 3ab\ P}}{bR}$$

10. Calculate the amount of heat needed to heat 200 grams of N_2O from 27°C at 227°C at constant pressure. Given that

$$Cp_{N_2O} = 7.0 + 7.3 \times 10^{-3}\ T1 - 9 \times 10^{-6} T^2 \text{ cal/mole}$$

Ans. 8670 cal.

11. Show that work of reversible expansion of a gas is maximum and of reversible compression of a gas is minimum.

12. Derive an expression in each of the following cases:

(*a*) Isobaric reversible expansion,

(*b*) Isothermal reversible expansion when pressures are known and when volumes are known for the initial and final states.

13. Why are C_p and C_v of a substance usually different? When will they be same? When will C_p be more than C_v and when will C_p be less than C_v?

Chapter 7

THERMOCHEMISTRY

7.1. INTRODUCTION

It is well known that reactions are accompained by the transfer of heat from reactants to surroundings or *vice versa.* Thermochemistry deals with the heat changes associated with chemical processes either at constant volume or at constant pressure. The subject has great practical utility as it give us information about the energy or enthalpy contents of compounds, a knowledge of which is necessary for the study of chemical bonding and chemical equilibria. The laws of thermochemistry are largely based on the first law. Unfortunately, the scope of thermochemistry is limited largely because only a very few of the several chemical reactions are such that their heats of reaction can be accurately measured. In order to know whether a given reaction can be subjected to a precise calorimetric study, it must satisfy the following criterion of: (*i*) fast; (*ii*) complete; and (*iii*) a clean reaction. We shall consider these criterion one after the other.

(1) **Fast reaction.** A reaction has to be fast because if the heat is to be given out or absorbed in a short period of time, it will be easier to prevent the transfer of heat from the reaction system or into it from the surroundings.

(2) **Complete reaction.** The reaction must go to completion, that is, all the reactants should be converted into products. This is necessary to avoid difficult corrections which have to be made for the unreacted material.

(3) **Clean reaction.** A clean reaction implies that the reactants should given only one set of products free from any side-reactions which might occur in addition to the main reaction. The side reactions interfere with the accurate calorimetric study of a chemical reaction.

The heat changes are usually expressed in kilocalories; abbreviated to kcal, where 1 kcal=1000 cal. and sometimes also in joule.

7.2. STANDARD STATE AND THE SIGN CONVENTION FOR HEAT TRANSFER

The value of enthalpy and internal energy will depend on the temperature and pressure for any given physical state. In order to standardise the data on heats of reaction, it is necessary that some reference point be established for the thermodynamic states of the reactants and products. The choice of such a reference point is just arbitrary and is called standard state of the substance. In thermochemistry, temperature of 25°C (298K) and pressure of 1 atm are generally used as standard conditions for all substances (pure solids, liquids and ideal gases). (More recently, the standard state is defined at pressure of 1 atm. and any specified temperature). The symbols *g*, *l* and *s* placed in the parentheses after the formula indicate whether the substance taking part in the reaction is gas, liquid or crystalline solid, respectively. Consider a general reaction represented as:

$$\text{Reactants} \longrightarrow \text{Products}$$

For this reaction the internal energy change and the enthalpy change are given by:

$$\triangle E = E_{\text{Products}} - E_{\text{Reactants}}$$
$$\triangle H = H_{\text{Products}} - H_{\text{Reactants}}$$

If the reactants and products are in the standard state, the heat transferred is called the standard heat for that reaction and $\triangle E$ and $\triangle H$ for such reactions are symbolised by $\triangle E^\circ$ and $\triangle H^\circ$ respectively. If heat is absorbed in a reaction, it is known as endothermic reaction and if heat is evolved in a reaction, it is described as exothermic reaction. *$\triangle H$ or $\triangle E$ will be positive, if heat is absorbed and negative, if heat is evolved.*

7.3. HEAT OF REACTION

It is the change in enthalpy when molar quantities of reactants shown by the balanced equation for the reaction react completely.

Consider the reaction in which one mole (12 g) of graphite combines with one mole (32 g) of gaseous oxygen given one mole (44 g) of gaseous carbon dioxide. In this reaction, 94.03 k. calories of heat are evolved. The reaction can be symbolised as:

$$C_{(s)} + O_{2(g)} = CO_{2(g)} \qquad \triangle H = -94.03 \text{ kcal.}$$

For a constant pressure process,

$$(\triangle H)_P = (\triangle E)_P + P\triangle V$$

For reactions involving only liquids and solids, since $\triangle V$ is very slight; $P\triangle V$ is usually negligible in comparison with $(\triangle E)_P$. Therefore, for reactions involving solids and liquids, the heat absorbed at constant pressure and constant volume are same for all practical purposes. For reactions involving gases

$$P\triangle V = \triangle_n RT$$

$$\therefore \qquad (\triangle H)_P = \triangle E + \triangle_n RT \qquad \ldots (7.1)$$

where $\triangle n$ is the change in the number of moles of gaseous products and reactants. Here it is assumed that the gases are ideal. Equation (7.1) is utilized in converting $\triangle H$ into $\triangle E$ and *vice versa*. This can be illustrated by considering the example given below:

Problem 7.1. When 1 mole of liquid benzene is completely burnt in oxygen to form liquid water and carbon dioxide gas, $\triangle H$ is -781.0 kcal at 25°C (298K). Calculate the heat of this reaction at constant volume at the same temperature.

Solution. For this reaction.

$$C_6H_6(l)+7\tfrac{1}{2}O_2(g)=3H_2O(l)+6H_2O(g)$$
$$\triangle H_{298}=-781.0 \text{ kcal.}$$

The number of moles n_A of gaseous reactants is 7.5, while the number of moles n_B of gaseous products is 6, so that

$$\triangle n=n_B-n_A=-1.5.$$

The temperature T is 298K, and R may be taken as 2 cal (or 2×10^{-3} kcal) $\text{deg}^{-1}\,\text{mole}^{-1}$

hence, from equation, $\triangle H=\triangle E+RT\,\triangle n$, we have

$$\triangle H=\triangle E-(2\times10^{-3}\times298\times1.5)$$
$$-981.0=\triangle E-0.9$$

or $$\triangle E_{298}=-780.1 \text{ kcal.}$$

This is the heat of reaction at constant volume.

7.4. THE LAWS OF THERMOCHEMISTRY

The two laws of thermochemistry are based on the principle of conservation of energy. The *first law* was given by *Lavoisier* and *Laplace* in 1780. It states as follows:

"*The quantity of heat which must be supplied to decompose a compound into its elements is equal to the heat evolved when the compound is formed from its elements.*"

Thus if the reverse of a chemical reaction is written, the sign of $\triangle H$ is changed, but its magnitude remains same. For example, the heat evolved when water is formed from hydrogen and oxygen is exactly equal to the heat absorbed when water decomposes into hydrogen and oxygen. The thermochemical equations can be symbolised as:

$$H_{2(g)}+\tfrac{1}{2}O_{2(g)}=H_2O_{(l)} \qquad \triangle H=-68300 \text{ cals.}$$
$$H_2O_{(l)}=H_{2(g)}+\tfrac{1}{2}O_{2(g)} \qquad \triangle H=+68300 \text{ cals.}$$

The other examples of this law are the following:

$$CO_{2(g)}+H_{2(g)}=CO_{(g)}+H_2O_{(g)} \qquad \triangle H=-680 \text{ cals.}$$
$$H_2O_{(g)}+CO_{(g)}=CO_{2(g)}+H_{2(g)} \qquad \triangle H=+680 \text{ cals.}$$
$$S_{(s)}+O_{2(g)}=SO_{2(g)} \qquad \triangle H=-70960 \text{ cals.}$$
$$SO_{2(g)}=S_{(g)}+O_{2(g)} \qquad \triangle H=+70960 \text{ cals.}$$

Hess's Law. This empirical law was put forward by Hess in 1940. According to this law, "*the overall heat change in a chemical reaction carried out either at constant pressure or at constant volume is the* *same, irrespective of the fact whether the reaction proceeds in one or several stages.*"

This is a direct consequence of the first law of thermodynamics, according to which $\triangle E$ and $\triangle H$ are equal to the heats of reaction at constant volume and constant pressure respectively and are dependent only on the initial and final states of system.

Suppose that we are provided with one mole of ammonia gas and one mole of hydrogen chloride and the aim is to get one litre of molar ammonium chloride solution and at the same time, we wish to measure the heat transfer in this process.

To start with, let us combine the gases to form the solid salt and then dissolve this salt in water. This can be symbolised as follows:

$$NH_3+HCl \longrightarrow NH_4Cl \qquad q=x \text{ kcal}$$

$$NH_4Cl+aq \longrightarrow NH_4Cl(M) \qquad q=y \text{ kcal}$$

where M stands for molar solution.

The overall heat transfer will be given by $(x+y)$ kcal. The other scheme for carrying out these reactions is given below:

$$NH_3+aq \longrightarrow NH_3\ (2M) \qquad q=z \text{ kcal}$$

$$HCl+aq \longrightarrow HCl\ (2M) \qquad q=r \text{ kcal}$$

$$NH_3(2M)+HCl(2M) \longrightarrow NH_4Cl(M) \qquad q=s \text{ kcal}$$

The overall heat transfer will be $(z+r+s)$ kcal. On comparing the overall heat transfer of the two results, it is found that

$$x+y=z+r+s$$

This proves Hess's law which may also be stated that *if different processes are used to bring about the same change, the heat change is same for all of them.*

The importance of Hess's law lies in the fact that heat changes can be calculated for reactions that cannot be performed in the laboratory. In these calculations, thermochemical equations can be added, subtracted, multiplied or divided algebraically. Some of the applications of Hess's law are:

(*i*) formation reactions of some compounds.

(*ii*) calculation of lattice energies of ionic crystals.

(*iii*) study of multistep reactions.

(*iv*) determination of calorific values of food and fuels.

Problem. 7.2. Determine $\triangle H$ for the reaction

$$2C+2H \longrightarrow C_2H_4 \qquad \triangle H_{25^\circ C}=?$$

given the experimental results

$$C+O_2 \longrightarrow CO_2 \qquad \triangle H_{25^\circ C}=-94 \text{ kcal} \qquad \ldots(i)$$

$$H_2+\tfrac{1}{2}O_2 \longrightarrow H_2O \qquad \triangle H_{25^\circ C}=-68.3 \text{ kcal} \qquad \ldots(ii)$$

$$C_2H_4+3O_2 \longrightarrow 2CO_2+2H_2O \qquad \triangle H_{25^\circ C}=-342 \text{ kcal} \qquad \ldots(iii)$$

Solution. If equations (*i*) and (*ii*) are multiplied by 2 and then added, we have

$$2C+2O_2 \longrightarrow 2CO_2 \qquad \Delta H_{25°C}=-2\times 94 \text{ kcal}$$
$$2H_2+O_2 \longrightarrow 2H_2O \qquad \Delta H_{25°C}=-2\times 68.3 \text{ kcal}$$

$$2C+2H_2+2O_2 \longrightarrow 2CO_2+2H_2O \qquad \Delta H_{25°C}=-324.6 \text{ kcal} \quad \ldots (iv)$$

Subtracting equation (*iii*) from equation (*iv*), we obtain the desired equation

$$2C+2H_2 \longrightarrow C_2H_4 \quad \Delta H_{25°C}=(-324.6+342)=+17.4 \text{ kcal}.$$

7.5. HEAT OF FORMATION

The thermal change involved in the formation of 1 mole of a substance from its elements is known as the *heat of formation* of the substance. If the reactants and products involved in the reaction are in the standard state (281 K and 1 atm), the heat change is referred to as the *standard heat of formation.*

In measuring heat of formation, a number of difficulties arise. To get around some of the difficulties, an assumption is made that *the enthalpies of all elements in their standard states at 25°C are arbitrarily taken to be zero.* If an element exists in more than one allotropic form under these conditions, the form most stable at 1 atm and 25°C is taken to have zero value.

Suppose you were to design an experiment to determine the heat of formation of carbon dioxide ($q°$) which is defined by the equation

$$C_{(s)}+O_{2(g)} \longrightarrow CO_{2(g)} \qquad q°=x\text{kJ}$$

In principle the method looks quite simple. You might decide to take a known weight of carbon and burn it in a stream of oxygen, transferring the heat to a calorimeter so that it can be measured. Now an important question arises—which allotrope of carbon will you choose and will the heat depend on the allotrope. Experiment shows that it does matter and in the case of carbon, graphite $C_{(gr)}$ and diamond $C_{(d)}$ to give different results, *i.e.*,

$$C_{(gr)}+O_{2(g)} \longrightarrow CO_{2(g)} \qquad q°=-393.51 \text{ kJ mole}^{-1}$$
$$C_{(d)}+O_{2(g)} \longrightarrow CO_{2(g)} \qquad q°=-395.41 \text{ kJ mole}^{-1}$$

From the equation

$$2Mg_{(s)}+O_{2(g)} \longrightarrow 2MgO_{(s)} \qquad q°=x \text{ kJ}$$

Calculate the standard heat of formation of magnesium oxide.

The equation shows that x kJ accompany the formation of two moles. Therefore the standard heat of formation will be $x/2$ kJ.

It is often possible to measure a heat of formation directly because the reaction will not work. If we want to find the heat of formation of potassium sulphate, we cannot put the elements together and measure the heat produced. The reaction,

$$2K_{(s)}+S_{(c)}+2O_{2(g)} \longrightarrow K_2SO_{4(s)} \qquad q°=y \text{ kJ}$$

will not work. It is because of this reason many heats of formation must be calculated using Hess's Law.

Generally speaking a compound that has a large heat of formation is unstable and one with a negative heat is stable. Consider the thermal stability of the hydrides of the halogens. When hydroiodic acid is warmed it breaks down quite readily forming appreciable quantities of hydrogen and iodine.

$$2HI \longrightarrow H_2 + I_2$$

Hydrogen bromide is more stable and hydrogen chloride is difficult to detect.

It is most important to distinguish between chemical reactivity and thermal stability. You will see that while calcium carbonate has a very low heat of formation, so that we would predict a high stability for it, (*i.e.*, the reaction,

$$2CaCO_{3(s)} \longrightarrow 2Ca_{(s)} + C_{(s)} + 3O_{2(g)}$$

will be a hard change to bring about) it is nevertheless quite reactive, for example,

$$CaCO_{3(s)} + 2HCl_{(g)} \longrightarrow CaCl_{2(s)} + H_2O_{(l)} + CO_{2(g)}$$

The problem is a common one because many elements show allotropy. It is therefore necessary to specify which allotrope is used for the synthesis of a compound and the normal practice is to use the most stable allotrope at the standard conditions. Table 7.1 gives the standard heat of formation of some common substances.

TABLE 7.1

Compound	*Standard heat of formation (kJ mol^{-1})*	*Compound*	*Standard heat of formation (kJ mol^{-1})*
$H_2O_{(g)}$	−241.82	$SO_{2(g)}$	−296.8
$H_2O_{(l)}$	−285.83	$H_2S_{(g)}$	−39.3
$NH_{3(g)}$	−46.11	$SF_{6(g)}$	−1209.00
$HNO_{3(l)}$	−174.1	$HCl_{(g)}$	−92.31
$H_2SO_{4(l)}$	−811.3	$HBr_{(g)}$	−36.4
$NaCl_{(s)}$	−412.1	$HI_{(g)}$	+26.5
$NaOH_{(s)}$	−425.6	$CO_{2(g)}$	−393.51
$KCl_{(s)}$	−435.6	$Al_2O_{3(s)}$	−1669.8
$NO_{(g)}$	+90.25	$SiO_{2(s)}$	−859.4
$NO_{2(g)}$	+33.2	$FeS_{(s)}$	−95.1
$N_2O_{4(g)}$	+9.16	FeS_2	−117.9

Problem 7.3. Calculate the standard heat of reduction of ferric oxide by aluminium which proceeds according to the following reaction.

$$2Al_{(s)}+Fe_2O_{3(s)}\rightarrow 2Fe_{(s)}+Al_2+Al_2O_{3(s)}$$

Given the heat of formation of $Fe_2O_{3(s)}$ and $Al_2O_{3(s)}$ are—196.5 kcal mole^{-1} and —399.1 kcal mole^{-1} respectively.

Solution. Let the heat of reduction of ferric oxide by aluminium be x kcal:

$$2Al_{(s)}+FeO_{3(s)}\rightarrow 2Fe_{(s)}+Al_2O_{3(s)} \qquad \triangle H^\circ = x \text{ kcal}$$

and $\triangle H^\circ = x = \left[2H^\circ_{Fe_{(s)}}+H^\circ_{Al_2O_{(s)}}\right]-\left[2H^\circ_{Al_{(s)}}+H^\circ_{Fe_2O_{3(s)}}\right]$

$$=(0-399.1)-(0-196.5)$$

$$=-202.6 \text{ kcal.}$$

Hence the standard heat of reduction

$$=-202.6 \text{ kcal.}$$

Problem 7.4. Calculate the heat of reaction for

$$CO_{(g)}+H_2O_{(l)}=CO_{2(g)}+H_{2(g)}$$

at 20°C from the given table of heats of formation

Chemical species	*Heat of formation* $\triangle H_f$ *(kcal mole^{-1})*
$H_2O_{(l)}$	—68.3
$CO_{(g)}$	—26.4
$CO_{2(g)}$	—94.0

Solution. Substitution in the given equation

$$CO_{(g)}+H_2O_{(l)}=CO_{2(g)}+H_{2(g)}$$

$$-26.4-68.3-94.00$$

gives for the reaction

$$\triangle H \text{ reaction} = H_{\text{products}} - H_{\text{reactants}}$$

$$=-94.0-[-26.4+(-68.3)]$$

$$=-94.0-(-94.7)$$

$$=-94.0+94.7=0.7 \text{ kcal}$$

$$\triangle H \text{ reaction} = 0.7 \text{ kcal at } 20^\circ\text{C.}$$

7.6. HEAT OF SOLUTION

When a substance is dissolved, heat may be either liberated or absorbed depending on the relative amounts of energy which are used up in breaking down the crystal lattice on the one hand and the energy liberated during the hydration of the solute on the other. The quantity of heat evolved is not constant but varies with the concentration of the final solution. This may be due to a number of factors, *e.g.*, the variation in the extent of hydration of the solute, and in some cases to the degree of dissociation.

The heat of solution is, therefore, defined as the amount of heat evolved when one mole of the solute is dissolved in a specified amount of solvent. For quantitative expression, the total heat change per mole of solute when solution is complete is called the *integral heat* *of solution.* Per mole of dissolved substance the integral heat of solution at any given temperature and pressure depends upon the number of moles of solvents in which solution takes place. This can be indicated as follows:

$$HCl_{(g)}+50H_2O_{(l)}=HCl(50H_2O) \quad \triangle H=-73KJ\ mole^{-1}$$

which means that when 1 mole of HCl is dissolved in 50 moles of water, 73 KJ of heat are evolved. If the final solution is very dilute (*i.e.*, such that further dilution would cause no additional heat change) the equation is written as

$$HCl_{(g)}+aq=HCl_{(aq)} \quad \triangle H=-75KJ\ mole^{-1}$$

where *aq* represents a large volume of water.

The corresponding △H value is called the heat of solution at infinite dilution and represents the upper limit of heat released when a substance is dissolved in a large excess of solvent.

The difference between any two integral heats of solution gives the heat involved in the dilution of solution from one concentration to another concentration, and is called the *integral heat of dilution.* Thus, the heat evolved on diluting HCl $(50H_2O)$ with a large quantity of water is

$$(HCl)(50H_2O)+aq=HCl(aq)$$
$$\triangle H=-75+73=-2KJ$$

i.e., in diluting HCl $(50H_2O)$ to infinite heat of solution, 2KJ of heat is given out.

Consider a general solution process in which n_2 moles of a solute are dissolved in n_1 moles of the solvent at any given temperature and pressure. Since the integral heat of solution depends on the amounts of both solvent and solute, we have

$$\triangle H=f(n_1, n_2)$$

or $$\partial(\triangle H)=\left[\frac{\partial(\triangle H)}{\partial n_1}\right]_{n_2} dn_1+\left[\frac{\partial(\triangle H)}{\partial n_2}\right]_{n_1} dn_2$$

Replacing $\left[\frac{\partial(\triangle H)}{\partial n_1}\right]_{n_2}$ by $\triangle \bar{H}_1$ and $\left[\frac{\partial(\triangle H)}{\partial n_2}\right]_{n_1}$ by $\triangle \bar{H}_2$,

we get $\partial(\triangle H)=\triangle \bar{H}_1 dn_1+\triangle \bar{H}_2 dn_2$

$\triangle \bar{H}_1$ and $\triangle \bar{H}_2$ are called the *partial* or *differential molal heats of solution* for the solvent and solute respectively. These cannot be measured directly but can be calculated from the integral heat of solution data.

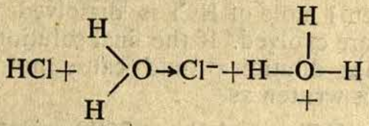
The differential heat of solution of the solvent is the difference between the $\triangle \bar{H}_1$, values for two different concentrations, namely,

$$(\triangle \bar{H}_1)_d=(\triangle \bar{H}_1)_2-(\triangle \bar{H}_1)_1$$

where the subscripts 1 and 2 outside the brackets represent, respectively, initial and final concentration. Similarly, the differential heat of solution of the solute is given by

$$(\Delta \bar{H}_2)_d = (\Delta \bar{H}_2)_2 - (\Delta \bar{H}_2)_1$$

Substances that dissolve with the liberation of heat do so because they react with water. Hydrogen chloride undergoes the change



where H_3O^+ can be regarded as a hydrated hydrogen ion.

Similarly,

$$H_2SO_4 + 3H_2O \rightarrow 2H_3O^+ + (SO_4.H_2O)^{2-}$$

where sulphate ion is also hydrated. Anhydrous salts give out heat too and for the same reason, anhydrous copper sulphate reacts to form hydrates of both ions present,

$$Cu^{2+}SO_4^{2-} + 5H_2O \rightarrow (Cu.4H_2O)^{2+} + (SO_4.H_2O)^{2-}$$

The formation of bond between water molecules and ions is always an exothermic process; although the nature of the bond depends on the ion. Anions link with water molecules by hydrogen bonding. Some cations link by cotonic bonds, other electrostatistically.

One the other hand, when a salt is dissolved in water and in the process of solution, no new species are formed, the process is endothermic as it is accompanied by the separation of ions, *e.g.*, solution of KI in water.

7.7. HEAT OF NEUTRALISATION

When aqueous solution of acids and bases react, heat is evolved. *The change in enthalpy when one gram equivalent of an acid is neutralised by one gram equivalent of a base in dilute solution is known as the heat of neutralisation of the acid.*

It has been shown that the heat of neutralisation of any strong acid by a strong base is practically the same as shown in the following reactions:

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O \qquad \Delta H = -13.7 \text{ kcal}$$

$$HNO_{3(aq)} + NaOH_{(aq)} \rightarrow NaNO_{3(aq)} + H_2O \qquad \Delta H = -13.7 \text{ kcal}$$

The constant value of —13.7 kcal for the heat of neutralisation of a strong acid with a strong base indicates that the same chemical change is taking place in all these reactions. The neutralisation of hydrochloric acid by sodium hydroxide can be symbolised as:

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$$

or

$$H^+ + OH^- \rightarrow H_2O \qquad \Delta H = -13.7 \text{ kcal}$$

Hence every neutralisation reaction involves the combination of H^+ and OH^- ions to form unionised water. However, the heat of neutralisation of a weak acid or a weak base is not constant. This can be explained on the ground that in such cases, in addition to neutralisation, the ionisation or dissociation of the weak acid or the weak base also takes place. For example, the neutralisation of acetic acid by sodium hydroxide solution:

$$CH_3COOH+NaOH \rightarrow CH_3COONa+H_2O \qquad \triangle H=-13.25 \text{ kcal} \ldots (i)$$

is in reality a two-stage process:

$$CH_3COOH \rightleftharpoons CH_3COO^-+H^+ \qquad \triangle H_2=D \qquad \ldots (ii)$$

where D is the heat of dissociation and

$$H^++OH^- \rightarrow H_2O \qquad \triangle H=-13.7 \text{ kcal} \ldots (iii)$$

The sum of equations (*ii*) and (*iii*) gives equation (*i*). Consequently,

$$-13.25=D+(-13.7)$$

or

$$D=+0.45 \text{ kcal}$$

Hence the heat of ionisation or heat of dissociation of a weak acid or a weak base can be determined from the heat of neutralisation data.

Problem 7.5. The heat of neutralisation of hydrocyanic acid by sodium hydroxide is —2.90 kcal/gm—equivalent at 25°C. Calculate its heat of ionisation.

Solution. The given reaction is

$$HCN+OH^- \rightarrow CN^-+H_2O \qquad \triangle H_{25°C}=-2.90 \text{ kcal.}$$

Let $\triangle H_i$ be the heat of ionisation of hydrocyanic acid.

$$HCN \rightleftharpoons H^++CN^- \quad \ldots (i) \qquad \triangle H_{25°C}=\triangle H_i$$

$$H^++OH^- \rightarrow H_2O \quad \ldots (ii) \qquad \triangle H_{25°C}=-13.7 \text{ kcal}$$

The sum of these two equations (*i*) and (*ii*) gives

$$\triangle H_i+(-13.7)=-2.90$$

or

$$\triangle H_i=+10.80 \text{ kcal.}$$

7.8. HEAT OF FORMATION OF IONS IN SOLUTION

Since the heat changes in ionic reactions depend on the ions in solution, it is convenient to use the heats of formation of ions rather than the heat of formation for the neutral molecule. The heats of formation of ions under standard conditions *i.e.*, when all the species are at unit activity, are obtained in the following way:

The standard heat of formation of one mole of water from hydrogen and hydroxyl ions (which is essentially equal to the heat of neutralisation of strong electrolyte) and the standard heat of formation of water from its elements are given by

$$H^+_{(aq)}+OH^-_{(aq)} \rightarrow H_2O_{(l)} \qquad \triangle H°=-13.7 \text{ kcal}$$

$$H_{2(g)}+\tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} \qquad \triangle H°=-68.3 \text{ kcal}$$

Reversing the first equation and combining it with the second gives

$$H_{2(g)}+\tfrac{1}{2}O_{2(g)}=H^+_{(aq)}+OH^-_{(aq)} \qquad \triangle H^\circ=-54.6 \text{ kcal} \quad \ldots (a)$$

This represents the sum of the heats of formation of a proton and hydroxyl in solution. In order to resolve this sum and to obtain heat of formation of single ion, an arbitrary convention is adopted. According to this convention, *the heat of formation of the hydrogen ion in aqueous solution is zero at 25°C and unit activity i.e., that for the reaction.*

$$\tfrac{1}{2}H_{2(g)}+aq=H^+_{(aq)} \qquad \Delta H^\circ_{25^\circ C}=0 \quad \ldots (b)$$

when equation (*b*) is subtracted from equation (*a*), one gets directly the heat of formation of the hydroxyl ion, or

$$\tfrac{1}{2}H_{2(g)}+\tfrac{1}{2}O_{2(g)}+aq=OH^-_{(aq)} \qquad \triangle H^\circ_{25^\circ C}=54.6 \text{ kcal}$$

Hence the heat of formation of OH^- is —54.6 kcal $mole^{-1}$. Once the heats of formation of these two ions are known, those for other ions can be readily calculated from reactions having measurable heat changes.

Problem 7.6. Calculate the standard heat of formation of chloride ions using the standard heat of formation of HCl in water at 25°C

$$\Delta H^\circ_{25^\circ C}=-40.02 \text{ kcal}$$

Solution. The given reaction is

$$\tfrac{1}{2}H_{2(g)}+\tfrac{1}{2}Cl_{2(g)}+aq=H^+_{(aq)}+Cl^-_{(aq)} \quad \Delta H^\circ_{25^\circ C}=-40.02 \text{ kcal.}$$

By combining it with the convention

$$\tfrac{1}{2}H_{2(g)}+aq=H^+_{(aq)} \qquad \Delta H^\circ_{25^\circ C}=0,$$

We get

$$\tfrac{1}{2}Cl_{2(g)}+aq=Cl^-_{(aq)} \qquad \triangle H^\circ_{25^\circ C}=-40.02 \text{ kcal}$$

which is the heat of formation of chloride ions.

Problem 7.7. Calculate the standard heat of formation of sodium ions in aqueous solution from the following reaction:

$$Na_{(s)}+\tfrac{1}{2}O_{2(g)}+\tfrac{1}{2}H_{2(g)}+aq=Na^+_{(aq)}+OH^-_{(aq)} \quad \triangle H^\circ_{25^\circ C}=-112.24 \text{ kcal}$$

Given that the heat of formation of hydroxyl ions in aqueous solution at 25°C is —54.6 kcal.

Solution. Given data:

$$Na_{(s)}+\tfrac{1}{2}O_{2(g)}+\tfrac{1}{2}H_{2(g)}+aq=Na^+_{(aq)}+OH^-_{(aq)} \quad \triangle H^\circ_{25^\circ C}=-112.24 \text{ kcal}$$

and $\tfrac{1}{2}H_{2(g)}+\tfrac{1}{2}O_{2(g)}+aq=OH^-_{(aq)}$ $\qquad \Delta H^\circ_{25^\circ C}=-54.6$ kcal

Combining these two equations, we get

$$-112.24 = \Delta H^\circ_{Na^+} + \Delta H^\circ_{OH^-}$$

$$= \Delta H^\circ_{Na^+} - 54.60$$

or $$\Delta H^\circ_{Na^+} = -112.24 + 54.60 = -57.64 \text{ kcal.}$$

Problem 7.8. Calculate the enthalpy change when infinitely dilute solutions of $CaCl_2$ and Na_2CO_3 are mixed under standard conditions. It is given that standard heat of formation of $Ca^{2+}_{(aq)}$, $CO^{2-}_{(aq)}$ and $CaCO_{3(s)}$ are -129.8, -161.63 and -288.45 kcal/mole respectively.

Solution. The reaction is

$$Ca^{2+}_{(aq)} + 2Cl^-_{(aq)} + 2Na^+_{(aq)} + CO_3^{2-}{}_{(aq)}$$

$$\longrightarrow CaCO_{3(s)} + 2Na^+_{(aq)} + 2Cl^-_{(aq)}.$$

Cancelling the heats of chloride and sodium ions which appear on both sides of the reaction, we get

$$Ca^{2+}_{(aq)} + CO_2^{2-}{}_{(aq)} \longrightarrow CaCO_{3(s)} \qquad \Delta H^\circ_{25^\circ C} = ?$$

$\Delta H^\circ_{25^\circ C}$ for this reaction is given as

$$\Delta H^\circ_{25^\circ C} = H^\circ CaCO_{3(s)} - \left[H^\circ Ca^{2+}{}_{(aq)} + H^\circ Ca_3^{2-}{}_{(aq)} \right]$$

Substituting the various values given, we get

$$\Delta H^\circ_{25^\circ C} = (-288.45) - [(-129.77) + (-161.63)]$$

$$= +2.95 \text{ kcal.}$$

7.9. HEAT OF COMBUSTION

The heat of combustion of a compound or element is the change of heat content when one mole of it is burnt in oxygen at constant pressure.

The heats of combustion depend on the conditions of burning. For example, if water is the product of combustion, the heat evolved will depend on whether it is in the liquid or vapor form. Thus it is essential to state the conditions of combustion and to have a standard heat. If one mole of a substance is completely burnt into oxygen, reactants and products being at 298K and 1 atm, the heat evolved is referred to as the standard heat of combustion. Standard heat of combustion are usually stated by means of an equation, for example,

$$C_6H_6 + 7\tfrac{1}{2}\, O_2 = 6CO_2 + 3H_2O \qquad \Delta H^\circ = -781.0 \text{ kcal}$$

This means that when one gram molecule of benzene is burnt in excess of oxygen, 781 kcal of heat are given out. The heat of com-

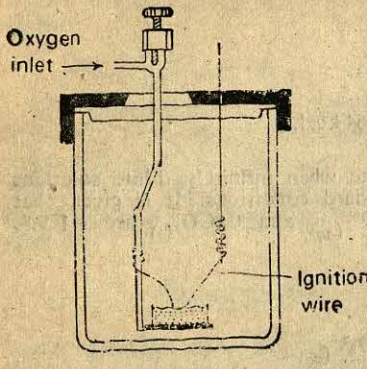


Fig. 7.1. Combustion bomb.

bustion can be determined experimentally in a Bomb calorimeter. The general form of this apparatus is shown in Fig. 7.1.

The substance whose heat of combustion is to be determined is placed on the platinum support and above it the two platinum wires are joined by a thin spiral of iron wire. The bomb is closed and oxygen is introduced till the pressure inside the bomb is about 25 atmospheres. The electric spark is then produced by which a large amount of heat is produced. This will raise the temperature of the water around the colorimeter. To start with, the apparatus is calibrated by the measurement of temperature rise resulting from the combustion of a sample with a known heat of combustion Generally a known weight of benzoic acid is taken, the heat of combustion of this compound being accurately known.

In organic chemistry, the combustion reactions are of outstanding suitability. The heat of combustion is also of great practical significance. Fuels are bought on their calorific values. The energy providing foods are classified by the amount of heat they liberate when they are 'burnt' in the body.

It has been observed that substances whose molecules contain the same atoms and similar linkages, have heat of combustion that are very nearly the same. This idea can be utilized for establishing the structure of organic compounds.

7.10. VARIATION OF HEAT OF REACTION WITH TEMPERATURE

The heat of a reaction, calculated from a table of standard heats of formation or obtained calorimetrically, corresponds to some one definite temperature. As reactions are carried out at various temperatures, it is very frequently necessary to know heats of reaction at temperatures other than those at which they were determined. Consider a general reaction:

$$\text{Reactants} \longrightarrow \text{Products}$$

The enthalpy of reaction is given by

$$\triangle H = H\ \text{Products} - H\ \text{Reactants}$$

Differentiating both sides of this equation with respect to temperature we get,

$$\left(\frac{\partial \triangle H}{\partial T}\right)_P = \left(\frac{\partial H \text{ Products}}{\partial T}\right)_P - \left(\frac{\partial H \text{ Reactants}}{\partial T}\right)_P$$

By definition of heat capacity at constant pressure (*see* section 6.12):

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

Therefore,

$$\left(\frac{\partial \triangle H}{\partial T}\right)_P = C_p \text{ Products} - C_p \text{ Reactants}$$

or
$$\left(\frac{\partial \triangle H}{\partial T}\right)_P = \triangle C_p \qquad \ldots (7.1)$$

Hence it is necessary to know the difference in heat capacities of the products and reactants in order to determine the variation of heat of reaction with temperature. This is known as *Kirchoff's equation*. Similarly, we can obtain the equation for the variation of $\triangle E$ with temperatures, namely

$$\left(\frac{\partial \triangle E}{\partial T}\right)_V = C_v \text{ Products} - C_v \text{ Reactants}$$
$$= \triangle C_v \qquad \ldots (7.2)$$

For a small range of temperature, $\triangle C_p$ can be taken as constant and equation (7.2) can be written as

$$\int d(\triangle H) = \int \triangle C_p dT \qquad \ldots (7.3)$$

The integration of equation (7.4) depends on whether $\triangle C_p$ is constant or temperature dependent. When $\triangle C_p$ is constant, then integration between the temperatures T_1 and T_2 yields

$$\int_{\triangle H_1}^{\triangle H_2} d(\triangle H) = \int_{T_1}^{T_2} \triangle C_p dT$$

$$\triangle H_2 - \triangle H_1 = \triangle C_p (T_2 - T_1)$$

or
$$\triangle H_2 = \triangle H_1 + \triangle C_p (T_2 - T_1) \qquad \ldots (7.4)$$

where $\triangle H_2$ is the heat of reaction at T_2 and $\triangle H_1$ is that at T_1.

However, when temperature interval is very large, $\triangle C_p$ is not constant, then

$$\int d(\triangle H) = \int \triangle C_p dT + \triangle H_o$$

or
$$\triangle H = \int \triangle C_p dT + \triangle H_o \qquad \ldots (7.5)$$

Here $\triangle H_o$ is a constant of integration. In order to evaluate the integral in equation (7.6), $\triangle C_p$ must be available as a function of the temperature. Generally, the heat capacities of gases vary with temperature as a function of power series of T *i.e.*

$$C_p=\alpha+\beta T+\gamma T_2+\delta T^3+\ldots$$

where α, β, γ, δ etc., are constants for the given gas and must be derived from the experimentally determined heat capacities over a range of temperature. For the general chemical reaction,

$$aA+bB+\ldots \longrightarrow lL+mM+\ldots$$

the overall change in the heat capacity, $\triangle C_p$, is thus given by

$$\triangle C_p=[l(C_p)_L+m(C_p)_M+\ldots]-[a(C_p)_A+b(C_p)_B+\ldots]$$

Here the C_p terms are the molar heat capacities of the species indicated.

Problem 7.9. The standard heat of formation of liquid water is −68.3 kcal at 25°C. Calculate the value at 100°C. The molar heat capacities at constant pressure in the given temperature range of $H_{2(g)}$, $O_{2(g)}$ and $H_2O_{(l)}$ are 6.89, 6.97 and 18.0 cal deg^{-1} $mole^{-1}$ respectively.

Solution. The reaction for the heat of formation of liquid water can be written as:

$$H_{2(g)}+\tfrac{1}{2}O_{2(g)}=H_2O_{(l)}$$

$$\triangle H^\circ_{25^\circ C}=-68.3 \text{ kcal}$$

$$\triangle C_p=18.0-[6.89+(\tfrac{1}{2}\times 6.97)]$$

$$=7.63\times 10^{-3} \text{ kcal deg}^{-1}$$

$$T_2-T_1=75$$

$$\triangle H_1=-68.3$$

From Kirchoff's equation,

$$\triangle H_2=-68.3+7.63\times 10^{-3}\times 75$$

or $$\triangle H_2=-67.7 \text{ kcal.}$$

Problem 7.10. From the following information:

(*i*) $4C_2H_5Cl_{(g)}+13O_{2(g)}$

$$=Cl_{2(g)}+8CO_{2(g)}+10H_2O_{(g)}$$

$$\triangle H_{298K}=-1229.6 \text{ kcal}$$

(*ii*) $C_2H_{6(g)}+3\tfrac{1}{2}O_{2(g)}=2CO_{2(g)}+3H_2O_{(g)}$

$$\triangle H_{298K}=-341 \text{ kcal}$$

Heat of formation per mole of $H_2O_{(g)}=-57.8$ kcal

Heat of formation per mole of $HCl_{(g)}=-21$ kcal.

(*a*) Calculate $\triangle H_{288K}$ for the reaction

$$C_2H_{6(g)}+Cl_{2(g)}=C_2H_5Cl_{(g)}+HCl_{(g)}$$

(*b*) Assuming $\triangle C_p$ for the first reaction to be −10 cal/deg., calculate $\triangle H_{398K}$

(*c*) Calculate $\triangle E_{298K}$ for the reaction.

Solution. Write the first reaction in backward direction:

$$10H_2O+8CO_2+2Cl_2=13O_2+4C_2H_5Cl \;\; \triangle H_1=1229.6 \text{ kcal.}$$

Multiplying equation (*ii*) by 4

$$4C_2H_6+14O_2=8CO_2+12H_2O \;\; \triangle H_2=-4\times 341 \text{ kcal.}$$

To get 4 moles of HCl

$$2Cl_2+2H_2=4HCl \;\; \triangle H_3=-4\times 21 \text{ kcal.}$$

Write the equation for the formation of water in backward direction

$$2H_2O=O_2+2H_2 \qquad \triangle H_4=2\times 57.8 \text{ kcal.}$$

Adding all these equations, we get

$$4C_2H_6+4Cl_2=4C_2H_5Cl+4HCl$$

$$\triangle H=1229.6-1364-84+115.6$$

$$=-103 \text{ kcal.}$$

(*b*) $\triangle H_{398K}=\triangle H_{298K}+\triangle C_p(T_2-T_1)$

$$=-1229.6-(10\times 100)/1000$$

or $\triangle H_{398K}=-1230.6$ kcal.

(*c*) $\triangle E_{298K}=\triangle H_{298K}-\triangle nRT$

$$=-1229.6-(20-17)\times 1.98+10^{-3}+298$$

$$\triangle E_{298K}=-1231.4 \text{ kcal.}$$

Problem 7.11. The standard heat of formation listed for gaseous NH_3 is -11.02 kcal/mole at 298K. Given that at 298K, the constant-pressure heat capacities of gaseous N_2, H_2 and NH_3 are respectively 6.96, 6.89 and 8.38 cal/mole, determine $\triangle H^\circ_{298k}$ and $\triangle H_{773k}$ for the reaction

$$\frac{1}{2}N_{2(g)}+\frac{3}{2}H_{2(g)}=NH_{3\,(g)}$$

Solution. For the reaction we can write,

$$\triangle H^\circ_{298K}=\triangle H^\circ_{NH_3}-0-0=-11.02 \text{ kcal/mole}$$

For the reaction that concerns us, at 298K,

$$\triangle C_p=8.38-\frac{1}{2}(6.96)-\frac{3}{2}(6.89)$$

$$=-5.43 \text{ cal/mole}$$

From equation

$$\triangle H_2=\triangle H_1+\triangle C_p(T_2-T_1)$$

We have

$$\triangle H^\circ_{773k}=\triangle H^\circ_{293k}+\triangle C_p(773-298)$$

$$=-11020+(-5.43)(475)$$

$$=-13600 \text{ cal/mole.}$$

7.11. THE TEMPERATURE OF FLAMES

A flame may be regarded as a region where gases are reacting to produce heat and often light. The heat produced raises the temperature of reactants and products within the flame. The gaseous products leave the flame with a high thermal energy and this is transferred to the surrounding air by molecular collisions. Such a transformation in which the heat produced is radiated to the surroundings is assumed to have taken place at a constant temperature. However, if a chemical reaction, *e.g.*, the combustion of gaseous hydrocarbons in oxygen or air, takes place under adiabatic conditions, the heat produced is not dissipated to the surroundings but is used to raise the temperature of the products sufficient to produce a flame. This temperature is called the *maximum flame temperature* and will depend on the amount of heat produced by the reaction. If the reaction takes place at constant volume, the quantity of heat liberated is denoted by ΔE and the maximum temperature is called

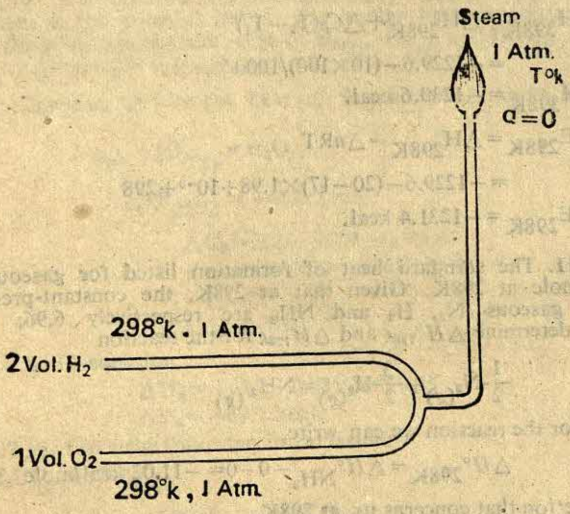


Fig. 7.2. The oxygen-hydrogen flame.

the *explosion temperature*. For a constant pressure process, the heat liberated is denoted by ΔH and the maximum temperature to which the products are raised is called the *flame temperature*. Consider the oxygen-hydrogen flame as is shown in Fig. 7.2.

The hydrogen and oxygen in the ratio of 2 moles and 1 mole are supplied to the burner at 298K and 1 atm pressure. The reaction occurs to produce steam at T K and 1 atm pressure. The steam then mixes with the air and its heat energy is radiated to the atmosphere. Ignoring the radiation from the flame, which is very little, the flame reaction can be written as

$$2H_2+O_2=2H_2O\ ;\ q=O$$

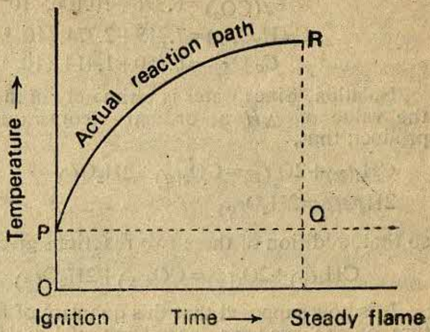


Fig. 7.3. Hess's law applied to flames.

In other words, heat produced is used to raise the temperature of the product and non-escapes. According to the Hess's law, the heat evolved in a change is independent of the route taken. Hence instead of considering the complex route present in the flame (*PR*), we construct a simple route $P \rightarrow Q \rightarrow R$ as shown in Fig. 7.3.

In the first stage, *PQ* represents the conversion of one mole of hydrogen and half a mole of oxygen both at standard conditions, to one mole of water at standard condition. In the second stage, *QR* represents the heating of one mole of water at 298K to TK. Utilising the principle that the overall heat radiation is zero, *T*, the temperature of flame is calculated which comes out around 10,000K. The measured temperature of an oxygen-hydrogen flame is found to be lower than this. This discrepancy in the observed and theoretical value is due to the fact that specific heats are not constant over a range of temperature and also, existence of molecular water is doubtful at very high temperature.

From a knowledge of heats of reactions and of the variations with temperature of the heat capacities of reactants and products, we can easily calculate the maximum flame temperature with the help of Kirchoff's equation written in the form

$$\triangle H_{(\text{heating})} = -\triangle H_{(\text{reaction})} = \int_{T_1}^{T_2} \Sigma(nC_p)dT$$

In this equation, we have taken $\triangle H_{(\text{heating})} = -\triangle H_{(\text{reaction})}$ because the heat required to raise the temperature of the products from initial temperature T_1 to the maximum flame temperature, T_2, is equal in magnitude to the heat of reaction, but opposite in sign. $\Sigma(nC_p)$ is the sum of the heat capacities of all the species present in the system when the reaction is complete. Similarly, it is possible to calculate explosion temperature by using $\triangle E$ and C_v exactly in the same manner as were used $\triangle H$ and C_p in the calculation of flame temperature.

Problem 7.12. The heat of combusion of methane is —212.8 kcal at 25°C; the difference in the heat contents of liquid water and vapor at 1 atm. pressure at 25°C is 10.52 kcal. Calculate the maximum temperature of the flame when one mole of methane is completely burnt in calculated amount of air (1 O_2 to $4N_2$) just sufficient for combustion at 25°C and a constant pressure. The necessary data of heat capacities and their temperature dependence are given on next page.

$$C_p(CO_2) = 6.396 + 10.100 \times 10^{-3} \quad T - 3.405 \times 10^{-6}\ T^2$$
$$C_p(H_2O,\ g) = 7.219 + 2.374 \times 10^{-3} \quad T + 0.2670 \times 10^{-6}\ T^2$$
$$C_p\ (N_2) = 6.450 + 1.414 \times 10^{-3} \quad T - 0.0808 \times 10^{-6}\ T^2.$$

Solution. Since water is ultimately in the gaseous form at high temperature, the value of ΔH at ordinary temperature is required with water vapor as the product; thus,

$$CH_1(g) + 2O_2(g) = CO_2(g) + 2H_2O(l) \qquad \Delta H_{298K} = -212.80 \text{ kcal}$$
$$2H_2O(l) = 2H_2O(g) \qquad \Delta H_{298K} = 2 \times 10.52 \text{ kcal}$$

so that, addition of these two reactions gives

$$CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(g) \qquad \Delta H_{298K} = -191.76 \text{ kcal}$$

It is now supposed that this quantity of heat is utilised to raise the temperature of the products, consisting of 1 mole CO_2, 2 moles H_2O and 8 moles of N_2 which were associated in the air with 2 moles of O_2 used in the combustion of 1 mole of CH_4. If T_2 is the maximum theoretical flame temperature to which the products are raised, then the heat requied to raise the temperature of the products from 25°C *i.e.*, 298K to T_2 must be equal in magnitude to the heat of reaction, but opposite in sign. From Kirchhoff's equation, using

$$\Delta H_{(\text{heating})} = -\Delta H_{(\text{reaction})} = 191{,}760 \text{ cal},$$

we have

$$191{,}760 = \int_{T_2}^{T_1} \Sigma(nC_p)dT$$

Here,

$$\Sigma(nC_p) = C_p(CO_2) + 2 \times C_p\ (H_2O;\ g) + 8 \times C_p\ (N_2)$$

Substituting the various values of heat capacities from the given data, we have

$$\Sigma(nC_p) = 72.43 + 26.15 \times 10^{-3}\ T - 3.517 \times 10^{-6}\ T^2 \text{ cal deg}^{-1}.$$

Inserting this into Kirchoff's equation,
we get

$$191{,}760 = \int_{298}^{T_1} (72.43 + 26.15 - 10^{-3}\ T - 3.517 \times 10^{-6}\ T^2)dT$$
$$= 72.43(T_2 - 298) + 13.08 \times 10^{-3}\ [T_2^2 - (298)^2]$$
$$-1.172 \times 10^{-6}\ [T_2^3 - (298)^3]$$

or $$214.470 = 72.43\ T_2 + 13.08 \times 10^{-3}\ T_2^2 - 1.172 \times 10^{-6}\ T_2^3$$

Solving this equation by the method of successive approximations, the value of T_2 is found to be about 2250 K or 1980°C.

7.12. BOND ENERGIES

A more fundamental approach to the problem of calculating heats of reaction for processes for which no thermal data is available is by the use of bond energies. By the bond energy is meant the average amount of energy per mole necessary to rupture a particular bond in a molecule and thus effect a complete separation of the resulting atoms or radicals from one another. For diatomic molecules like H_2, O_2, N_2, Cl_2 or a molecule like *AB*, this energy is called as *bond dissociation energy* and is easily measured by spectroscopic methods. Bond energy and bond dissociation energy are equivalent only for diatomic molecules. In a polyatomic molecule, the energy required to break a given bond will depend to some extent on the nature of the remainder of the molecule and will vary from compound to compound. For instance, the energy required to break the O—H bond in an alcohol is not the same as the energy needed to break the same bond in an organic acid. The bond energy in a polyatomic compound is the average amount of energy required to break a particular bond in one mole of the compound. For example, in the water molecule, we have

$$H_2O_{(g)}=H_{(g)}+OH_{(g)} \qquad \triangle H_{298k}=119.95 \text{ kcal mole}^{-1}$$

On the other hand, to break the O—H bond in the hydroxyl radical requires a different heat quantity

$$OH_{(g)}=O_{(g)}+H_{(g)} \qquad \triangle H_{298k}=101.19 \text{ kcal.}$$

The bond energy e_{O-H} will be the average of these two values *i.e.*,

$$e_{O-H}=\frac{119.95+101.19}{2}=110.57 \text{ kcal mole}^{-1}.$$

In the case of diatomic molecules, such as H_2, the bond energy and the bond dissociation energy are identical, for both refer to the following reaction:

$$H_{2(g)}=2H_{(g)},\ e_{H-H}=\triangle H_{298K}=104.18 \text{ kcal.}$$

In order to determine the bond energy for a particular bond such as the C—H bond, we first determine the enthalpy change for the following reaction:

$$CH_{4(g)}=C_{(g)}+4H_{(g)}$$

Let $\triangle H$ be the enthalpy change for this reaction. If we call the bond energy of C—H as e_{C-H} then

$$e_{C-H}=\frac{\triangle H}{4}$$

($\because$ there are four C—H bonds and all the bonds are identical). From the heat of combustion data, $\triangle H$ for CH_4 was found to be 398.0 kcal. Therefore

$$e_{C-H}=\frac{398.0}{4}$$

$$=99.5 \text{ kcal mole}^{-1}$$

Similarly, bond energies for the H—O, H—N, H—S bond can be determined from the heats of reactions in which the molecules H_2O, NH_3 and H_2S are formed from their atoms. When a bond breaks, bond enthalpy is positive. But, when a bond is formed, bond enthalpy is negative.

It is important to appreciate what is meant by one bond. The symbols H_2, Cl_2, N_2 refer to one mole of the substance which contains 6.023×10^{23} molecules. Thus one mole of hydrogen chloride contains 6.023×10^{23} linkages and one mole of ammonia contains $3 \times 6.023 \times 10^{23}$ linkages. The energy to break one H—H bond actually means the energy to break all the linkages in a mole of the gas.

In diamond the carbon atoms are arranged in such a manner that each atom has four neighbours placed at the corners of a tetrahedron. Each carbon atom is linked to its neighbours by covalent bonds as shown in Fig. 7.4.

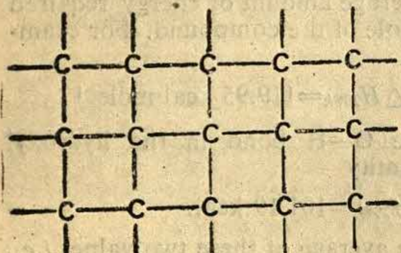


Fig. 7.2. The structure of diamond in two diamensions.

To calculate the bond energy e_{C-C}, we proceed as follows:

The heat required to vaporise carbon is measured from the following reaction:

$$C_{(solid)} \longrightarrow C_{(gas)}$$

$\triangle H = +160$ kcal.

From the above figure we see that in order to produce one mole of carbon atoms, twice this number of C—C bonds must be broken. Therefore, the bond energy e_{C-C} is $+80$ kcal. Table 7.1 gives the results of bond energies for various bonds.

TABLE 7.2

Bond Energy Data (in kJ mol^{-1})

Bond	*Bond energy*	*Bond*	*Bond energy*
C—C	348	N—H	331
C=C	610	N—N	861
C≡C	826	N—O	175
H—H	436	N=N	
H—F	563	O—H	463
H—Cl	432	O—O	140
H—Br	366	S—S	339
H—I	299	F—F	153
C—H	413	Cl—Cl	243
C—Cl	328	I—Cl	210
C—O	350	I—Br	178
C=O	732	N—Cl	200
C—N	292	Si—Si	177

Uses of Bond Energies

The concept of bond energy is very useful and finds number of user in chemistry. The important uses are:

(*a*) comparing the strengths of bonds,

(*b*) understanding structure and bonding,

(*c*) estimating the enthalpy changes in reactions, and

(*d*) understanding the mechanisms of chemical reactions.

The most important application of bond energies is their use in estimating the enthalpy changes in chemical reactions. These estimations are particularly useful when calorimetric or other experimental measurements can not be made.

Problem 7.13. Given that the bond enthalpies for C—H, Cl—Cl, C—Cl and H—Cl are respectively 99, 58, 78 and 103 kcal/mole, determine ΔH for the reaction:

$$CH_{4(g)} + Cl_{2(g)} = CH_3Cl_{(g)} + HCl_{(g)}$$

Solution. In this reaction, the three C—H bonds in CH_4 are unaffected and they may thus be neglected. Only one C—H bond in CH_4 and one H—H bond in H_2 are broken. In turn, one C—Cl bond in CH_3Cl and one H—Cl bond in HCl are formed. Therefore,

$$\Delta H_{25°C} = -(e_{C-Cl} + e_{H-Cl}) + (e_{C-H} + e_{Cl-Cl})$$

Inserting the various values, we get

$$\Delta H_{25°C} = -(78+103)+(99+58)$$

$$\Delta H_{25°C} = -24 \text{ kcal.}$$

PROBLEMS

1. What is meant by the heat of a reaction? Outline one method by which the heat of a reaction can be determined. Of what value is a knowledge of the heat of a reaction?

2. State Hess's law of constant Heat Summation and show that it is a direct consequence of the first law of thermodynamics.

3. Discuss the use of Hess's law in calculating heats of reaction that are difficult to determine experimentally.

4. Define the terms (*a*) Heat of formation; (*b*) Heat of hydration; (*c*) Heat of neutralisation.

5. Calculate the enthalpy of formation of $Ca(OH)_2(s)$ from the following data:

$H_{2(g)} + \frac{1}{2}O_{2(g)} = H_2O_{(l)}$ $\Delta H = -68.3$ kcal

$CaO_{(s)} + H_2O_{(l)} = Ca(OH)_{2(s)}$ $\Delta H = -15.3$ kcal

$Ca_{(s)} + \frac{1}{2}O_{2(g)} = CaO_{(s)}$ $\Delta H = -151.8$ kcal

Ans. -235.4 **kcal**

6. Define the term heat of combustion. Give one method for its determination.

Ethanol was oxidised to acetic acid in a catalyst chamber at 18°C. Calculate the rate of removal of heat to maintain the reaction chamber at 18°C with a feed rate of 30 kg per hour ethanol (plus excess oxygen) to the system at 18°C, given that a 42 mole per cent yield (based on ethanol) is obtained. Given that:

$$\Delta H_{f\,298K}[H_2O(l)] = -68.4 \text{ kcal mole}^{-1}$$
$$\Delta H_{f\,291K}[C_2H_5OH(l)] = -66.0 \text{ kcal mole}^{-1}$$
$$\Delta H_{f\,291K}[CH_3COOH(l)] = -118.0 \text{ kcal mole}^{-1}$$

Ans. 32,970 kcal hr^{-1}

7. Calculate the heat of formation of aluminium chloride which exists as dimer (Al_2Cl_6) in the solid, from the heat of reaction of the following reactions:

$$Al_{(s)} + 3HCl_{(aq)} = AlCl_{3\,(aq)} + \tfrac{3}{2}H_{2(g)} \qquad \Delta H^\circ = -125.4 \text{ kcal}$$
$$\tfrac{1}{2}H_{2(g)} + \tfrac{1}{2}Cl_{2(g)} = HCl_{(g)} \qquad \Delta H^\circ = -22.05 \text{ kcal}$$
$$HCl_{(g)} + aq = HCl_{(aq)} \qquad \Delta H^\circ = -17.96 \text{ kcal}$$
$$\tfrac{1}{2}Al_2Cl_{6(s)} + aq = AlCl_{3(aq)} \qquad \Delta H^\circ = -77.9 \text{ kcal}$$

8. For the hydrogenation of cyclohexene to form cyclohexane at 82°C according to the reaction

$$C_6H_{10(g)} + H_{2(g)} = C_6H_{12(g)}$$

$\Delta H_{355K} = -28.6$ kcal $mole^{-1}$. Calculate the heat of hydrogenation of benzene to cyclohexane at 82°C. The experimental value is -49.8 kcal $mole^{-1}$, explain the discrepancy. **Ans.** -85.8 kcal.

9. Deduce the relation for the study of variation of heat of reaction with temperature.

10. Calculate the heat of vaporisation of H_2O at 120°C, and 1 atm pressure. The heat capacity of $H_2O(l)$ may be taken as 1.0 cal/g-degree, C_p for vapor as 0.45/g-degree, and the heat of vaporisation at 100°C as 540 cal/g. **Ans.** 529 cal/g.

11. Explain what is meant by term "bond energy." How can the bond energy data be used to assign the correct structure to a molecule?

12. By using bond energies, calculate the approximate heat of formation of ethane. The reaction is,

$$2C(s) + 3H_2(g) = C_2H_6(g)$$

Ans. -19 kcal.

13. The heat of formation of ammonia at 18°C and 1 atm pressure is $-11{,}020$ cal $mole^{-1}$. Calculate its heat of formation at 320°C. Given that

$$C_p(N_2, g) = 6.76 + 0.606 \times 10^{-3}T + 1.3 \times 10^{-7}T^2 \text{ cal deg}^{-1} \text{ mole}^{-1}$$
$$C_p(H_2, g) = 6.62 + 0.81 \times 10^{-3}T \text{ cal deg}^{-1} \text{ mole}^{-1}$$
$$C_p(NH_3, g) = 6.70 + 6.30 \times 10^{-3}T \text{ cal deg}^{-1} \text{ mole}^{-1}$$

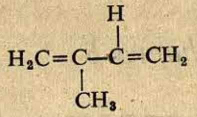
Ans. $-12{,}390$ cal $mole^{-1}$

14. On the basis of the following data, evaluate the standard enthalpy of formation of tungsten carbide, $WC(s)$

$$C(g) + O_2(g) = CO_2(g) \qquad \Delta H^\circ_{298k} = -94.052 \text{ kcal}$$
$$WC(g) + \frac{5}{2}O_2(g) = WO_3(s) + CO_2(g) \qquad \Delta H^\circ_{298k} = -285.80 \text{ kcal}$$
$$WC(s) + \frac{3}{2}O_2(g) = WO_3(s) \qquad \Delta H^\circ_{298k} = -290.16 \text{ kcal}$$

Ans. 8.41 kcal.

15. Using the bond energy data given below, estimate the heat of formation of gaseous isoprene



$$H_2C=\underset{\displaystyle CH_3}{\underset{|}{C}}-\overset{\displaystyle H}{\overset{|}{C}}=CH_2$$

Given that:

Bond energy of C—H bond $= 98.8$ kcal mole^{-1}

Bond energy of C—C bond $= 83.1$ kcal mole^{-1}

Bond energy of C=C bond $= 147.0$ kcal mole^{-1}

Heat of sublimation carbon (graphite) $= 171.7$ kcal mole^{-1}

Heat of dissociation of $H_2(g)$ $= 104.2$ kcal mole^{-1}

16. In a typical experiment, using a bomb calorimeter, the bomb and the inner container are warmed by 5 1365°C when 105.60 kcal of heat is generated electrically. Calculate the heat capacity of the calorimeter. If 10.165 g of carbon in the form of graphite is burned in the calorimeter and a temperature increase of 3.8718° is produced, calculate the heat of formation of carbon dioxide.

Ans. 20.559 kcal deg^{-2}
94.05 kcal deg^{-1}

Chapter 8

ENTROPY: THE SECOND LAW OF THERMODYNAMICS

8.1. SPONTANEOUS PROCESSES

Although the First Law of Thermodynamics establishes the relationship between the various types of heat changes and work performed, it does not tell us about the source of heat or the direction of heat flow. It simply requires that the total energy is conserved whenever any change takes place. Thus, according to first law, it is possible to transfer heat from a lower to a higher temperature without any external aid. But in actual practice, it is not so. Instead, heat always flows spontaneously from a warmer to a colder body. Experience tells that (*a*) water runs downhill, (*b*) petroleum vapors and oxygen, when reminded by a small spark of their chemical obligations, react in a car engine to produce a mixture of exhaust gases, (*c*) the electricity tends to flow from a point of higher potential to one of low, (*d*) if aqueous solutions of NaCl and $AgNO_3$ are mixed, AgCl is formed spontaneously.

Now must we ask ourselves, why the opposite process of the ones mentioned above do not occur? That is, can water flow of itself upwards? Can carbon dioxide and water vapors congregate to form petroleum and oxygen? If electricity can flow from lower potential to a higher potential? All these questions are foolish questions because these things have never happened. However, from these observations we find that *all naturally occurring processes always tend to change spontaneously in a direction which will lead to equilibrium and are unidirectional.* The second law sums up our experience with equilibria just as the first law sums up our experience with energy.

A process is said to be reversible if during the change the system, is always in equilibrium and the change proceeds infinitely slowly. For a reversible change the work done by the system is maximum, *i.e.* ,$w_{rev} > w_{irr}$ and $q_{rev} > q_{irr}$. Thus during a reversible change, a system absorbs maximum heat from its surroundings and performs the maximum work on the surroundings.

8.2. THE SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics can be stated in a number of ways. The original statements were concerned with the French engineer Sadi Carnot's analysis of performance of steam engines. There are two important statements of the second law; one is due to Lord Kelvin and other is due to Clausius: The statement due to Kelvin may be expressed as:

> *It is impossible for a cyclic process to take heat from a cold reservoir and convert it into work without at the same time transferring heat from a hot to a cold reservoir.*

The statement due to Clausius is:

> *It is impossible to construct a machine, which is able to convey heat by a cyclic process from one reservoir at a lower temperature to another at higher temperature unless work is done on the machine by some outside agency.*

A cycle is a process in which a system returns to its original state after a succession of steps. A more useful statement of the second law can be given in terms of a quantity which is also a function of state called, *entropy*.

8.3. THE CARNOT CYCLE

It was pointed out by Carnot that even an ideal engine, operating under ideal conditions, cannot completely convert absorbed heat into work. Only a fraction of the absorbed heat is converted into work and that this fraction is determined by the operating temperatures, θ_H and θ_L, and does not depend on the nature of the engine. To prove this, Carnot considered a hypothetical engine which converts heat into work by a cyclic process. The engine consists of a cylinder fitted with a weightless and frictionless piston and containing a given weight of any 'working' substance. Two heat reservoirs which remain at constant temperature *viz.*, θ_H (upper) and θ_L (lower) respectively are also available. The Carnot cycle consists of four steps:

(1) Isothermal expansion;

(2) Adiabatic expansion;

(3) Isothermal compression; and

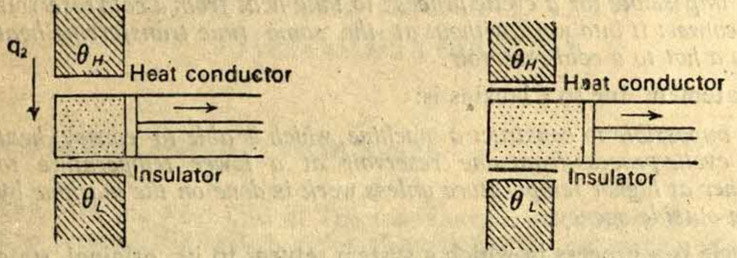
(4) Adiabatic compression.

A diagrammatic representation of the four stages of Carnot cycle is given in Fig. 8.1.

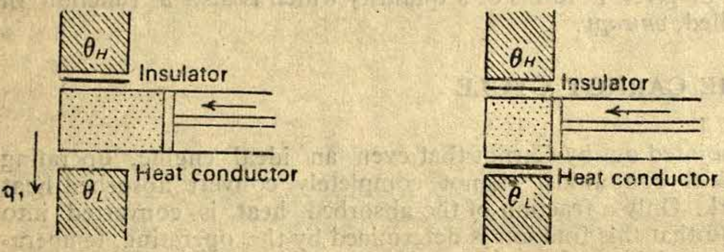
Step 1. The gas cylinder is placed in the heat reservoir maintained at temperature θ_H and the gas is expanded isothermally and reversibly from an initial volume V_1 to a volume V_2. The pressure also changes from P_1 to P_2.

In doing so. the system absorbs q_2 calories of heat from the constant temperature bath. This heat goes to increase its internal energy by $\triangle E_1$ and performs the work W_1. According to the first law, we have then

$$\triangle E_1 = q_2 - W_1 \qquad \ldots (8.1)$$



Stroke 1: Isothermal Expansion Stroke 2: Adiabatic Expansion



Stroke 3: Isothermal Compression Stroke 4: Adiabatic Compression

Fig. 8.1. Carnot engine.

Step 2. The cylinder is then taken out of the reservoir, insulated and is allowed to expand reversibly and adiabatically to volume V_2 while the temperature of the system will drop to θ_L. Since no heat is transferred; $q=0$. According to first law,

$$\triangle E_2 = -W_2 \qquad \ldots (8.2)$$

Step 3. The insulation is removed and the cylinder is now placed in a constant temperature bath maintained at temperature θ_L and the substance is compressed isothermally and reversibly from V_3 to V_4. Now q_1 calories of heat flow from the substance to the cold reservoir and work W_3 is done on the system.

Hence

$$\triangle E_3 = -q_1 - W_3 \qquad \ldots (8.3)$$

Step 4. The cylinder is removed from the reservoir and insulated again. The substance is compressed reversibly and adiabatically from the volume V_4 to the original volume V_1. The substance performs the amount of work W_4 and the temperature of the system rises from θ_L to θ_H as it returns to its original state. This being an adiabatic process, $q=0$ and so we have

$$\triangle E_4 = -W_4 \qquad \ldots (8.4)$$

The cyclic nature of the whole process can best be seen with the help of a *P-V* diagram, known as an "indicator diagram" in Fig. 8.2.

The step 1 takes the substance from state *A* to *B* in an isothermal reversible expansion. The step 2 takes the substance from *B* to *C* in the reversible adiabatic expansion. The step 3, involving the isothermal reversible compression, takes the substance from state *C* to state *D*. Finally the step 4, involving the adiabatic reversible compression of the substance takes it from state *D* to state *A*.

As a result of these four stages, the system has returned to its original state, so that a reversible cycle has been completed. The total change in energy for the complete cycle is given by

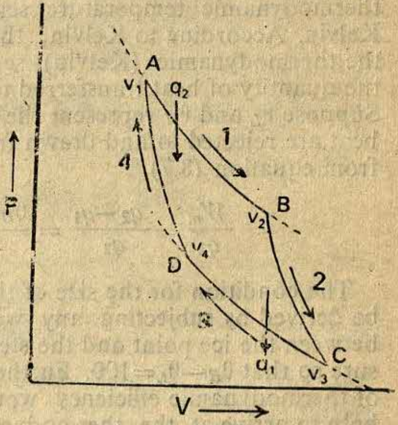


Fig. 8.2. *P-V* diagram forCarnot's cycle.

$$\begin{aligned}\triangle E &= \triangle E_1 + \triangle E_2 + \triangle E_3 + \triangle E_4\\ &= (q_2 - W_1) - W_2 - (q_1 + W_3) - W_4\\ &= (q_2 - q_1) - (W_1 + W_2 + W_3 + W_4)\\ &= (q_2 - q_1) - W_m \qquad \ldots (8.5)\end{aligned}$$

where W_m is the net work done in the complete cycle. Further, since for a cyclic process, the sum of internal energy for the whole process will be zero, the net work is given by

$$W_m = q_2 - q_1 \qquad \ldots (8.6)$$

It can be seen that only a portion of the heat taken in from the hot reservoir can be converted into work. Further, since efficiency of a machine is defined as the fraction of heat absorbed at the higher temperature by the engine that it can convert into work, it follows on dividing both sides of equation (8.6) by q_2 that

$$\epsilon = \frac{W_m}{q_2} = \frac{q_2 - q_1}{q_2} \qquad \ldots (8.7)$$

where ε is the *thermodynamic efficiency* of the Carnot cycle. It follows from equation (8.7) that the efficiency of an engine is always less than unity, since q_1 is less than q_2. This is another way of stating the fact that no engine can be constructed which can completely convert all the heat energy supplied to it into work. Equation (8.7) further shows that ϵ is independent of the nature of the working substance and is determined only by q_2 and q_1.

This result is of fundamental importance because its use leads to the definition of a temperature scale which does not depend on the arbitrary fixed points of a thermometric substance for its definition and therefore, holds for all substances. This scale is called the thermodynamic temperature scale and was first given by Lord Kelvin. According to Kelvin, the temperature of each reservoir on the thermodynamic (Kelvin) scale is defined as proportional to the quantity of heat transferred to or from it in a reversible cycle. Suppose θ_L and θ_H represent the temperatures at which quantities of heat are rejected to and drawn from cold and hot reservoirs. Then, from equation (8.7)

$$\frac{W_m}{q_2}=\frac{q_2-q_1}{q_2}=\frac{\theta_H-\theta_L}{\theta_H} \quad \ldots (8.8)$$

The condition for the size of the degree on the Kelvin scale may be derived by subjecting any working substance to a Carnot cycle between the ice point and the steam point at one atmospheric pressure so that $\theta_H-\theta_L=100$. Further, from equation (8.8), knowledge of thermodynamic efficiency would enable one to find θ_H and thus help to arrive at the thermodynamic temperature corresponding to the steam point. Knowledge of θ_H would also fix θ_L, the ice point of water and one would then obtain the ice point on the thermodynamic scale.

Actually, it will be seen shortly that θ-values, on the absolute thermodynamic scale of temperature, are directly proportional to T-values on an ideal-gas temperature. If then it is agreed that 273.16° is also to represent θ_L-value for the ice point of water, it is assured that the absolute scale will everywhere coincide with the ideal-gas law. This is proved by taking an ideal gas as the working substance and subjecting it to a Carnot cycle.

Carnot cycle for ideal gases. If one mole of an ideal gas is used as the working substance in a Carnot cycle between the temperatures T_2 and T_1 corresponding to θ_H and θ_L, then we have in line with Fig. 8.2, the scheme of Table 8.1.

For the complete cycle, sum of the internal energy will be zero and the net work done W will be given by $W=q_2-q_1$. Further,

$$W=W_1+W_2+W_3+W_4$$

$$W=RT_2\,ln\left(\frac{V_2}{V_1}\right)+\int_{T_2}^{T_1} C_v dT+RT_1\,ln\left(\frac{V_4}{V_3}\right)+\int_{T_1}^{T_2} C_v dT$$

TABLE 8.1

Step no.	*General case*	*Ideal gas*
1.	$\Delta E_1 = q_2 - W_1$	$\Delta E_1 = 0,\ W_1 = q_2 = RT_2 \ln\left(\frac{V_2}{V_1}\right)$
2.	$\Delta E_2 = -W_2$	$\Delta E_2 = -W_2 = -\int_{T_2}^{T_1} C_v\, dT$
3.	$\Delta E_3 = -q_1 - W_3$	$\Delta E_3 = 0,\ W_3 = -q_1 = RT_1 \ln\left(\frac{V_4}{V_3}\right)$
4.	$\Delta E_4 = -W_4$	$\Delta E_4 = -W_4 = -\int_{T_1}^{T_2} C_v\, dT$

$$W = RT_1 \ln\left(\frac{V_2}{V_1}\right) + RT_1 \ln\left(\frac{V_4}{V_3}\right) \qquad \ldots (8.9)$$

In this cyclic process, q_2 is the heat absorbed from the hot reservoir and q_1 is the heat returned to the cold reservoir. Hence the heat absorbed by the system is $(q_2 - q_1)$ and this is equal to the network done by the system.

$$\text{Therefore, } W = q_2 - q_1 = RT_2 \ln\left(\frac{V_2}{V_1}\right) + RT_1 \ln\left(\frac{V_4}{V_3}\right) \qquad \ldots (8.10)$$

Equation (8.10) can be simplified by realizing that in Fig. 8.2, V_2 and V_3 are the end points on the adiabatic curve BC and V_1 and V_4 are the end points on the adiabatic curve AD.

Hence, by equation (6.59)

$$T_2 V_2^{\gamma-1} = T_1 V_3^{\gamma-1} = T_2 V_1^{\gamma-1} = T_1 V_4^{\gamma-1}$$

On dividing the first of these equations by the second, we get

$$\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_4}\right)^{\gamma-1}$$

or
$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

Inserting this result in equation (8.10), we have

$$W = q_2 - q_1 = RT \ln\left(\frac{V_2}{V_1}\right) - RT_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$W = R(T_2 - T_1) \ln \frac{V_2}{V_1} \qquad \ldots (8.11)$$

and the efficiency is given by

$$\frac{W}{q_2}=\frac{q_2-q_1}{q_2}=\frac{R(T_2-T_1)\ ln\left(\frac{V_2}{V_1}\right)}{RT_2\ ln\left(\frac{V_2}{V_1}\right)}$$

$$\eta=\frac{T_2-T_1}{T_2} \qquad \ldots(8.12)$$

It is obvious from equation (8.12) that the efficiency of a Carnot cycle can never be unity since for the efficiency to reach unity, T_1 must be equal to zero. Since this temperature can never be attained, therefore, it follows that no engine can have 100 per cent efficiency. In other words, 100 per cent conversion of heat into work is impossible in any cyclic process. It also follows from equation (8.12) that in order to increase the efficiency, one must use as low a sink temperature (T_1) and as high a source temperature (T_2) as possible. Furthermore, the thermodynamic efficiency must be the same for all reversible processes operating under given temperature conditions. This is referred to as Carnot Theorem. Equation (8.12) can be used to estimate the maximum conversion of heat into work for a real engine. This is very useful in engineering and explains why internal combustion engines with their high temperatures have more efficiency than steam engines.

Further, on comparing equation (8.12) with equation (8.8), we find that

$$\frac{\theta_H-\theta_L}{\theta_H}=\frac{T_2-T_1}{T_2}$$

or

$$\frac{\theta_L}{\theta_H}=\frac{T_1}{T_2} \qquad \ldots(8.13)$$

It follows from equation (8.13) that θ—values, on the absolute thermodynamic scale of temperatures, are directly proportional to T-values on an ideal-gas temperature scale. From this fact, it follows that the thermodynamic and ideal gas temperature scales are really the same and may be used for all substances.

Problem 8.1. An ideally operating refrigerator works between 0°C and T°C. It will freeze 1 kg of ice per hour (that is, remove 80 kcal of heat per hour at 0°C). At the same time, the total heat output to the room is 100 kcal/bour. Calculate the value of T°C.

Solution. Since we have a relation,

$$\frac{q_1}{T_1}=\frac{q_2}{T_2}$$

or

$$T_2=\left(\frac{q_2}{q_1}\right)T_1$$

Substituting the various values

$$T_2=\left(\frac{100}{80}\right)\times 273$$

$$T_2=341\text{ K}$$

or

$$T_2=68°\text{C}.$$

Problem 8.2. A steam engine in a nuclear power plant operates between 800 K and 330 K. What is the maximum work that can be obtained from 1 kWh of heat?

A household refrigerator operates between 373 K and 273 K. How many joules of heat can in principle be removed per kilowatt hour of work? A heat pump used to heat up a building operates between an inside temperature of 295 K and an outside temperature of 273 K. How much work must in principle be expended for every kilowatt hour of heat?

Solution.

$$W=q_1\,\frac{T_1-T_2}{T_1}=\frac{(1\ \text{kWh})(470\ \text{K})}{800\ \text{K}}=0.588\ \text{kWh}$$

$$q_2=W_1\,\frac{T_2}{T_1-T_2}=\frac{(1\ \text{kWh})(273\ \text{K})}{100\ \text{K}}$$

$$=(2.73\ \text{kWh})(10^3\ \text{Js}^{-1}\ \text{kW}^{-1})(60\ \text{mh}^{-1})(60\ \text{sm}^{-1})$$

$$=9.828\times10^6\ \text{J}$$

$$W=q_1\,\frac{T_1-T_2}{T_1}=\frac{(1\ \text{kWh})(22\ \text{K})}{295\ \text{K}.}=0.0746\ \text{kWh}$$

Problem 8.3. A heat engine operating between 1,000°C and 25°C produces work that is entirely used to run a refrigerating machine operating between 0°C and 25°C. Calculate the ratio of the heat absorbed by the engine to that absorbed by the refrigerator, assuming ideal operation for both.

Solution. The work produced by the engine, w

$$=q_1+q_2=\frac{q_2(T_2-T_1)}{T_2}$$

where $T_2=273+1000$

$$=1273\ \text{K}$$

$$T_1=273+25$$

$$=298\ \text{K}$$

$$\therefore\qquad w=\frac{q_2(1273-298)}{1273}$$

For the refrigerator,

$$w'=q_1'+q_2'$$

$$=q_1'\,\frac{(T_1'-T_2')}{T_1'}$$

where $T_1'=273+25=298$ K

$$T_2'=273$$

$$\therefore\qquad w'=\frac{q_1'(298-273)}{273}$$

Since $w=w'$,

We have

$$\frac{q_2(1273-298)}{1273}=\frac{q_1'(298-273)}{273}$$

hence

$$\frac{q_2}{q_1'}=\frac{25}{273}\times\frac{1273}{975}=0.12.$$

8.4. ENTROPY

For any substance subjected to Carnot cycle operating reversibly between temperatures T_2 and T_1, we have

$$\frac{W}{q_2}=\frac{q_2-q_1}{q_2}=\frac{T_2-T_1}{T_2}$$

or $$1-\frac{q_1}{q_2}=1-\frac{T_1}{T_2}$$

or $$\frac{q_2}{T_2}+\left(\frac{-q_1}{T_1}\right)=0 \quad \ldots (8.14)$$

As one isothermal and one adiabatic changes are involved, equation (8.14) is the algebraic sum of the $\frac{q}{T}$ terms where q_2 is the heat absorbed reversibly by the system at T_2 and $-q_1$, the heat absorbed at the temperature T_1. It may also be noted from equation (8.14) that the sum of the ratios $\frac{q}{T}$ around a closed path is zero.

It can be shown that any reversible cyclic process may be regarded as made up of a large number of Carnot cycles and the sum of the entropy changes for the various cycles must equal to zero. Consider for example, a reversible cyclic process being represented by *abcd* in Fig. 8.3. This may be approximated by Carnot cycles. The changes *abc* and *cda* may be regarded as a grid of isotherms and adiabatics. The grid can be used to construct a set of Carnot cycles so that the outer parts of the set trace out a curve that approximates the general Carnot cycle. If we were to carry out all these Carnot cycles the net result would be the same as perform ing the cyclic process *abcd*.

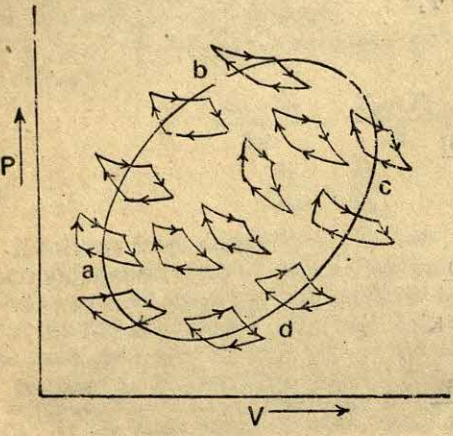


Fig. 8.3. A cyclic process approximated by a set of Carnot cycles.

This is so because the Carnot cycles that are inside the boundary cancel out because each is traced in both forward and in the reverse direction. If one goes to the limit of an infinitely closely spaced grid, one can obtain an exact reproduction of any process. Thus for a reversible cyclic process performed on an ideal gas, we have

$$\sum_{\text{Cycle}}\frac{q_{rev}}{T}=0 \quad \ldots (8.15)$$

where q_{rev} represents the various heats absorbed divided by the temperatures at which the absorption of heat occurs. Σ means the summation of $\frac{q_{rev}}{T}$ terms in all the Carnot cycles in which the process is divided. Equation 8.15 can also be writted as

$$\oint \frac{dq_{rev}}{T}=0 \qquad \ldots (8.16)$$

where $\oint$ signifies the integration around a complete cycle, and dq_{rev} is the heat absorbed in an infinitesimal small process carried out reversibly.

Definition of entropy. Mathematically, it follows from equation (8.16) that as the cyclic integral vanishes, the integrand must be a perfect differential of some function of state of the system. This function was named 'entropy' by Clausius for the first time and denoted by the symbol S. The actual entropy of a system is not easily defined, it is rather more convenient to define the change in the entropy, dS, for an infinitesimal stage of an appreciable reversible process which takes place by taking δq_{rev} calories of heat at constant temperature as

$$dS=\frac{\delta q_{rev}}{T} \qquad \ldots (8.17)$$

where T is the temperature in absolute. If heat enters a body, δq_{rev} is positive, and the entropy change is positive.

For any appreciable change, the change in entropy, $\triangle S$, when a system goes from the initial state a to the final state b at a constant temperature T is given by

$$\triangle S=S_b-S_a=\int_a^b \frac{\delta q_{rev}}{T} \qquad \ldots (8.18)$$

Since entropy, like the energy, is a function of state, dS, like dE, is a complete differential. S is thus independent of the past history of the system and can be expressed in terms of thermodynamic parameters (P, V, T). The entropy of a system, like the energy, is an extensive property, dependent upon the amount of matter in the system.

Units. Entropy has units of calories per degree and often stated as "entropy unit" (e.u.).

8.5. ENTROPY CHANGE IN A REVERSIBLE PROCESS

We have seen that for a reversible process, as for example in a Carnot cycle, total entropy change of the system must be zero since it has returned exactly to its original thermodynamic state. Hence, as expressed by equation (8.15)

$$\sum_{\text{cycle}} \frac{q_{rev}}{T} = 0$$

for the system. This result takes into consideration only the substance or substances included in the system and does not refer to the surroundings. In calculation of entropy changes, both the system and the surroundings must be taken into consideration. (The surroundings most frequently consist of heat reservoirs that can add to, or subtract heat from the system of mechanical devices which can do work on or accept work from the system). The combination of the system and its surroundings correspond to an isolated system.

In order to calculate entropy changes of systems and surroundings for a reversible isothermal process, consider an isolated system which consists of a cylinder containing any working substance and fitted with a frictionless and weightless piston. In order to maintain constant temperature, the cylinder is enclosed in a large heat reservoir which is thoroughly insulated from its surroundings. Let the temperature of the isolated system be constant and equal to T and suppose the working substance expands reversibly and isothermally from volume V_1 to V_2. During this process, the working substance will absorb a quantity of heat q_r from the surroundings.

Therefore, entropy change of the system is given by

$$\triangle S_{\text{system}} = \frac{q_r}{T}$$

However, at the same time, heat lost by surroundings is equal to q_r. Hence, entropy change of the surroundings is given by

$$\triangle S_{\text{surroundings}} = -\frac{q_r}{T}$$

The total change of entropy, $\triangle S_{\text{expansion}}$, during expansion is then given by

$$\triangle S_{\text{expansion}} = \triangle S_{\text{system}} + \triangle S_{\text{surroundings}}$$

$$= \frac{q_r}{T} - \frac{q_r}{T} = 0 \qquad \text{. . . (8.19}a\text{)}$$

If the working substance is now compressed reversibly and isothermally from V_2 back to V_1, the heat lost by the system will be q_r and so will be the heat gained by the surroundings. The entropy changes involved are

$$\triangle S'_{\text{system}} = \frac{-q_r}{T}$$

$$\text{and } \triangle S'_{\text{surroundings}} = \frac{q_r}{T}$$

and the total change of entropy, $\Delta S_{\text{compression}}$, during compression is then given by

$$\Delta S_{\text{compression}} = \Delta S'_{\text{system}} + \Delta S'_{\text{surroundings}}$$

$$= \frac{-q_r}{T} + \frac{q_r}{T} = 0 \qquad \ldots (8.19b)$$

Further, the total entropy change for the complete cycle, ΔS_{total}, is given by

$$\Delta S_{\text{total}} = \Delta S_{\text{expansion}} + \Delta S_{\text{compression}} = 0 \qquad \ldots (8.20)$$

The above considerations lead to the following two very important conclusions:

(*i*) *The entropy change of the system and surroundings together in a reversible, isothermal process is always zero.*

(*ii*) *The total entropy change for a reversible isothermal cycle is zero i.e.*, at the end of the cycle, the system has the same entropy as it had in the initial stage.

8 6. ENTROPY CHANGE IN AN IRREVERSIBLE PROCESS

When heat flows from high to low temperature or a gas expands in vacuum, it is observed that these processes occur spontaneously and are thermodynamically irreversible. All natural processes are more or less irreversible. The driving force that causes reactions to proceed spontaneously is the lack of balance in these processes. We can define irreversible processes as those which have a natural tendency to occur. These processes are spontaneous.

In order to calculate entropy change for any irreversible process, advantage is taken of the fact that the entropy change of the system depends only on the initial and final states and not on the path of the reaction.

Consider an isothermal and irreversible expansion of the substance from volume V_1 to V_2. During this process, let q be the amount of heat absorbed by the substance. The work done by the substance (W) during its irreversible expansion is less than that done in a reversible compression (W_{rev}). The heat absorbed q will also be less than heat absorbed (q_r) for a reversible expansion. Since the heat change in a process depends on the path adopted, the heat taken up irreversibly can have any value between $q=0$ and $q=q_r$, *i.e.*, the maximum value is that for a reversible process. But ΔS, being

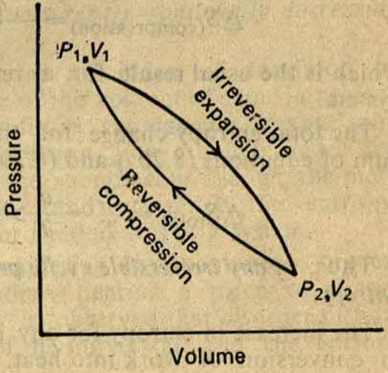


Fig. 8.4. Entropy change for a cycle containing an irreversible step.

a function of state, will have only one value for a change between the same initial and final states irrespective of how the process is carried out. Thus, we have

$$\Delta S_{irr},\ V_1 \rightarrow V_{2(\text{system})} = \Delta S_{rev},\ V_1 \rightarrow V_{2(\text{system})} = \frac{q_r}{T}.$$

However, the loss of heat q from the surroundings is considered to have taken place reversibly and so the entropy change of the surroundings is

$$\Delta S_{\text{surroundings}} = \frac{-q_r}{T}$$

Therefore, the total entropy change for the isothermal irreversible expansion of the substance is

$$\Delta S_{(\text{expansion})} = \Delta S_{(\text{system})} + \Delta S_{(\text{surroundings})}$$

$$= \frac{q_r}{T} - \frac{q}{T} < 0 \text{ (since } q_r > q) \qquad \ldots (8.20a)$$

Hence, an irreversible process occurring isothermally in an isolated system leads to an increase in the total entropy of the system.

In order to complete the cycle, the substance is returned to its original state by compressing it reversibly and isothermally from V_2 to V_1. In order to accomplish this, work is done on the substance and the amount of heat, q_r, produced is returned to the surroundings. The net result is that the change in entropy of the working substance will be equal to $\frac{-q_r}{T}$ and the entropy change of the surroundings will be $\frac{q_r}{T}$. Therefore, total change of entropy during reversible, isothermal compression is given by

$$\Delta S_{(\text{compression})} = -\frac{q_r}{T} + \frac{q_r}{T} = 0 \qquad \ldots (8.20b)$$

which is the usual result for a reversible process in an insolated system.

The total entropy change for the irreversible cycle will be the sum of equations (8.20a) and (8.20b) *i.e.*,

$$\Delta S_{\text{total}} = \frac{q_r}{T} - \frac{q}{T} > 0 \qquad \ldots (8.21)$$

Thus, *in any irreversible cyclic process, there is an increase in the entropy.*

The increase in entropy for any irreversible cyclic process is due to conversion of work into heat. At the end of the cycle, since the working substance has returned to its original state, it suffers no change of any kind. However, the surroundings lost heat equal to q, in the irreversible expansion but gained heat equal to q_r in the reversible compression. The net heat gained by the reservoir is thus $(q_r - q)$ and hence its entropy gain is $\left(\frac{q_r}{T} - \frac{q}{T}\right)$ a quantity greater than zero. At the same time, the work performed by the working substance in the irreversible expansion is W while that performed on the working substance in W_m. Thus the net work in cycle is $(W - W_m)$ which is less than zero since $W_m > W$. A negative value of the net work indicates that this work was done on the working substance and this resulted in the liberation of heat which was taken up by the surroundings; thus causing an entropy increase in the surroundings.

The statements of equations (8.20) and (8.21) are also valid for non-isothermal processes.

8.7. ENTROPY AND THE SECOND LAW (MOLECULAR INTERPRETATION OF ENTROPY)

From our previous discussion, it has been concluded that for any reversible process, $\triangle S = 0$ and for any irreversible process, $\triangle S > 0$.

Since all natural processes are spontaneous and irreversible, they must occur with an increase of entropy and therefore, the sum total of the entropy in the universe is continually increasing.

This conclusion permits a statement of the 2nd law of thermodynamics in its most general form, namely

"*The entropy of the universe always increases and tends toward a maximum.*"

On the other hand, the first law of thermodynamics states that the energy of the universe is constant. Thus the two laws of thermodynamics are often stated as:

First Law: *The energy of the universe is constant.*

Second Law: *The entropy of the universe is continually increasing and tends to a maximum.*

Entropy may be looked upon as an index of condition or character rather than as a measure of the content of some imaginary fluid. It is an index of the capacity for a spontaneous change and may be defined as an index of exhaustion. For example, more the system has lost its capacity for the spontaneous change, the more this capacity has been exhausted and greater is the entropy. Entropy is a measure of disorder or randomness of a system.

This can be easily proved by considering any spontaneous process *e.g.*, diffusion of one gas into another, heating a piece of copper metal etc. In all such cases, it is observed that disorder of final state is greater than the disorder of the initial state and the entropy change for the process is positive.

It has been found that sometimes there is a local fall in entropy in an open system. Photosynthesis provides an interesting example of a local fall in entropy. Before the reaction starts, both the reactants have high entropy. Carbon dioxide molecules move at random in the air; water molecules are mixed in the ground. After the reaction has occurred, the products are large molecules possessing a high degree of order. Thus there is a fall in entropy. However, this fall in entropy is compensated by changes in the sun which provides light energy and by other changes in the surroundings.

It is now possible to explain on a molecular level that why heat energy cannot be completely converted to other energy forms. From kinetic theory of gases, we know that heat energy is associated with the average kinetic energy of the randomly moving gas molecules. When the temperature is increased, average kinetic energy of the molecules also increases. It can be seen from Fig. 8.5 (*a*) that in order to convert the heat energy, *i.e.*, the kinetic energy of the molecules completely into mechanical energy, all the molecules must strike the piston perpendicularly. But, it does not happen so. Since the molecules are distributed in a random manner, they will strike the piston at all angles, as shown in Fig. 8.5(*b*). This results in less work being obtained than in the extremely rare case in which all the molecules are directed perpendicularly against the piston. Thus it can be concluded that all the heat energy cannot be completely converted into useful work. The heat energy which is not available to do the useful work at a constant temperature is directly related to the randomness or entropy of the system and is given by $q=TdS$.

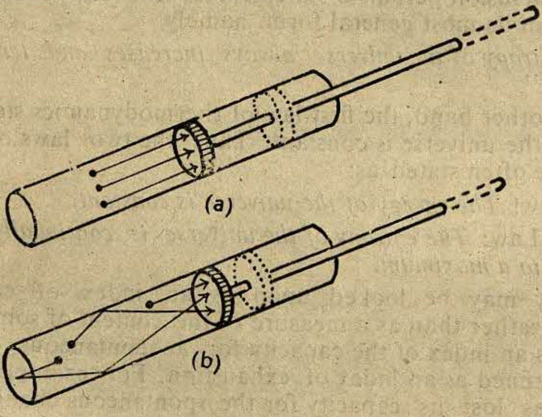


Fig. 8.5. (*a*) Complete conversion and (*b*) incomplete conversion of heat energy into mechanical energy.

8.8. DEPENDENCE OF ENTROPY ON VARIABLES OF A SYSTEM

Since the entropy, like energy, is a function of the state of a system, its value for any pure substance will be determined by any two of the three variables P, V and T. The variation of entropy with any of the three variables is given below:

(*i*) **Entropy as a function of temperature and volume.** If the entropy of a substance is a function of T and V, we have $S=f(T, V)$ and its differential is written as

$$dS=\left(\frac{\partial S}{\partial T}\right)_V dT+\left(\frac{\partial S}{\partial V}\right)_T dV \qquad \ldots (8.22)$$

Again, from the first law, for a reversible process, we have

$$dE=q_{rev}-W_{rev}$$
$$q_{rev}=TdS \text{ and } W_{rev}=PdV$$
$$dE=TdS-PdV \qquad \ldots (8.23)$$

Further, since $E=f(T, V)$

Therefore, its total differential is written as

$$dE=\left(\frac{\partial E}{\partial T}\right)_V dT+\left(\frac{\partial E}{\partial V}\right)_T dV \qquad \ldots (8.24)$$

Substituting dE from equation (8.23) into equation (8.24), we get

$$TdS-PdV=\left(\frac{\partial E}{\partial T}\right)_V dT+\left(\frac{\partial E}{\partial V}\right)_T dT$$

or

$$dS=\frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT+\frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T+P\right]dV \ldots (8.25)$$

Since both the equations (8.22) and (8.25) express the change of entropy in terms of changes in T and V, they are identical. On comparing these two equations, we get

$$\left(\frac{\partial S}{\partial T}\right)_V=\frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V \qquad \ldots (8.26a)$$

$$=\frac{C_v}{T} \qquad \ldots (8.26b)$$

and

$$\left(\frac{\partial S}{\partial V}\right)_T=\frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T+P\right] \qquad \ldots (8.27)$$

Since $\frac{C_v}{T}$ is always positive, equation (8.26*b*) predicts that at constant volume, the entropy increases with increase in temperature.

Again, rearranging equations (8.26*a*) and (8.27), we get

$$\left(\frac{\partial E}{\partial T}\right)_V=T\left(\frac{\partial S}{\partial T}\right)_V \qquad \ldots (8.28)$$

and

$$\left(\frac{\partial E}{\partial V}\right)_T=T\left(\frac{\partial S}{\partial V}\right)_T-P \qquad \ldots (8.29)$$

Differentiating equation (8.28) with respect to V at constant T and equation (8.29) with respect to T at constant volume, we get

$$\frac{\partial^2 E}{\partial T.\partial V}=T\left(\frac{\partial^2 S}{\partial T.\partial V}\right) \qquad \ldots (8.30)$$

and
$$\frac{\partial^2 E}{\partial T.\partial V}=T\left(\frac{\partial^2 S}{\partial T.\partial V}\right)+\left(\frac{\partial S}{\partial V}\right)_T-\left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots (8.31)$$

Since the order of differential is immaterial, equations (8.30) and (8.31) can be compared which yields,

$$\left(\frac{\partial S}{\partial V}\right)_T=\left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots (8.32)$$

Substituting equations (8.26*b*) and (8.32) in equation (8.22), we get

$$dS=\frac{C_v}{T}\,dT+\left(\frac{\partial P}{\partial T}\right)_V dV \qquad \ldots (8.33)$$

(*ii*) **Entropy as a function of temperature and pressure.** If the entropy of a substance is considered as a function of T and P, we have $S=f(T, P)$ and its total differential is written as:

$$dS=\left(\frac{\partial S}{\partial T}\right)_P dT+\left(\frac{\partial S}{\partial P}\right)_T dP \qquad \ldots (8.34)$$

Complete differential of the equation, $H=E+PV$, yields

$$dH=dE+PdV+VdP \qquad \ldots (8.35)$$

But, since from equation (8.23), $dE+PdV=TdS$, we have

$$dH=TdS+PdV \qquad \ldots (8.36)$$

Further, $H=f(T, P)$ and its differential is given by

$$dH=\left(\frac{\partial H}{\partial T}\right)_P dT+\left(\frac{\partial H}{\partial P}\right)_T dP \qquad \ldots (8.37)$$

Eliminating dH between equations (8.36) and (8.37), we have

$$dS=\frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P dT+\frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T-V\right] dP \qquad \ldots (8.38)$$

Since equations (8.34) and (8.38) are identical, they can be compared and hence we get

$$\left(\frac{\partial S}{\partial T}\right)_P=\frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P \qquad \ldots (8.39a)$$

$$=\frac{C_p}{T} \qquad \ldots (8.39b)$$

and
$$\left(\frac{\partial S}{\partial P}\right)_T=\frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T-V\right] \qquad \ldots (8.40)$$

Since $\frac{C_p}{T}$ is always positive for any substance, it follows from equation 8.39(*b*) that at constant pressure, the entropy increases with temperature.

Again, rearranging equations (8.39*a*) and (8.40), we obtain

$$\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P \quad \ldots (8.41)$$

and $$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V \quad \ldots (8.42)$$

Differentiating equation (8.41) with respect to P at constant T and equation (8.42) with respect to T at constant P, we get

$$\frac{\partial^2 H}{\partial T.\partial P} = T\left(\frac{\partial^2 S}{\partial T.\partial P}\right) \quad \ldots (8.43)$$

and $$\frac{\partial^2 H}{\partial T.\partial P} = T\left(\frac{\partial^2 S}{\partial T.\partial P}\right) + \left(\frac{\partial S}{\partial P}\right)_T + \left(\frac{\partial V}{\partial T}\right)_P \quad \ldots (8.44)$$

Since the order of differential is immaterial, equations (8.43) and (8.44) can be compared and we get

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \ldots (8.45)$$

Inserting equations (8.39*b*) and (8.45) in equation (8.34), we get

$$dS = \frac{C_p}{T}dT - \left(\frac{\partial V}{\partial T}\right)_P dP \quad \ldots (8.46)$$

Equations (8.33) and (8.46) are perfectly general and are equally applicable to pure solids, liquids or gases.

8.9. ENTROPY CHANGES FOR AN IDEAL GAS

For a reversible process consisting of an ideal gas and involving only the pressure-volume work, we have from the first law,

$$q_{rev} = dE + PdV \quad \ldots (8.47)$$

Again for 1 mole of an ideal gas, P is equal to $\frac{RT}{V}$ and $dE = C_v dT$. Therefore, equation (8.47) takes the form,

$$q_{rev} = C_v dT + RT\frac{dV}{V} \quad \ldots (8.48)$$

Dividing equation (8.48) throughout by T, we have

$$\frac{q_{rev}}{T} = C_v\frac{dT}{T} + R\frac{dV}{V}$$

But $$\frac{q_{rev}}{T} = dS$$

Therefore $$dS = C_v\frac{dT}{T} + R\frac{dV}{V} \quad \ldots (8.49)$$

This equation gives the total change in entropy for 1 mole of an ideal gas in a reversible process involving both a temperature and a volume change respectively.

On integration between the limits T_1, V_1 and T_2, V_2 (Initial and final temperature and volume respectively), we get

$$\triangle S=S_2-S_1=C_v\int_{T_1}^{T_2}\frac{dT}{T}+R\int_{V_1}^{V_2}\frac{dV}{V}$$

$$=C_v ln\frac{T_2}{T_1}+R\ ln\frac{V_2}{V_1} \qquad \ldots (8.50)$$

In carrying out the first integration on the right hand side, it is assumed that C_v is constant over the temperature interval in the equation. If, however, C_v is not constant, then it has to be substituted as a function of T and the expression integrated between the limits T_1 and T_2.

Again, for an ideal gas, $P_1V_1=RT_1$ for the initial state and $P_2V_2=RT_2$ for the final state. Therefore,

$$\frac{V_2}{V_1}=\frac{T_2P_1}{T_1P_2}$$

Substituting this in equation (8.50), we get

$$\triangle S=S_2-S_1$$

$$=C_v\ ln\frac{T_2}{T_1}+R\ ln\frac{T_2}{T_1}-R\ ln\frac{P_2}{P_1} \qquad \ldots (8.51)$$

Further, for 1 mole of an ideal gas

$$C_p-C_v=R \text{ or}$$

$$C_p=C_v+R$$

and $\triangle S=S_2-S_1=C_p\ ln\ \frac{T_2}{T_1}-R\ ln\frac{P_2}{P_1}$ $\qquad \ldots (8.52)$

We have some cases of particular interest.

Case I. For an isothermal process, since there is no change in temperature *i.e.*, T_1 is equal to T_2, equations (8.50) and (8.51), therefore, take the form

$$(\triangle S)_T=R\ ln\ \frac{V_2}{V_1}=-R\ ln\ \frac{P_2}{P_1} \qquad \ldots (8.53)$$

If $V_2>V_1$, $(\triangle S)_T$ will be positive from equation (8.53).

Case II. For a process taking place at constant pressure *i.e.*, P_1 and P_2 are equal, equation (8.52) takes the form

$$(\triangle S)_P=C_p\ ln\ \frac{T_2}{T_1} \qquad \ldots (8.54)$$

This process is also known as isobaric process.

Case III. For a process occurring at constant volume, equation (8.50) gives us:

$$(\triangle S)_V = C_v \ ln \frac{T_2}{T_1} \qquad \ldots (8.55)$$

Such a process is known as isochoric process.

Problem 8.3. 100 g of ice at 0°C is dropped into an insulated beaker containing 150 g of water at 100°C. Calculate $\triangle S$ for the process that occurs. Given that the heat of fusion of ice to be 80 cal/g, and the heat capacities of water and ice to be 1.0 and 0.5 cal/deg respectively.

Solution. The overall process can be written as the sum of the following three:

I. 100 g (ice, 0°C) = 100 g (water, 0°C),

$$q_1 = 100 \times 80$$
$$= 8000 \text{ cals.}$$

II. 100 g (water, 0°C) = 100 g (water, t°C),

$$q_2 = 100 \times t$$

III. 150 g (water, 0°C) = 150 g (water, t°C),

$$q_3 = -150\,(100 - t)$$

Since

$$q_{\text{total}} = 0$$
$$q_1 + q_2 + q_3 = 0$$
$$8000 + 100\,t - 150\,(100 - t) = 0$$

or

$$8000 + 250\,t - 15000 = 0$$
$$250\,t = 7{,}000$$
$$t = 28°\text{C}$$
$$301 \text{ K.}$$

The corresponding entropy changes are

$$\triangle S_1 = \frac{800}{273} = 29.3 \text{ e.u.}$$

$$\triangle S_2 = C_v \ ln \frac{T_2}{T_1}$$
$$= 100 \times 2.303 \ \log \left(\frac{301}{273}\right) = 9.7 \text{ e.u.,}$$

and

$$\triangle S_3 = C_v \ ln \frac{T_2}{T}$$
$$= 150 \times 2.303 \ \log \left(\frac{301}{373}\right)$$
$$= -32.1.$$

The overall $\triangle S$ is then

$$29.3 + 9.7 - 32.1 = 6.9 \text{ cal deg}^{-1}.$$

Problem 8.4. A sample of hydrogen is confined to a cylinder fitted with a piston of 5 cm^2 cross-section. It occupies 500 cm^3 and at room temperature it exerts a pressure of 2 atm. What is the change of entropy of the gas when the piston is drawn through 100 cm.

Solution. For an ideal gas $n = PV/RT$

$$\therefore \quad n = (2 \text{ atm})(5 \times 10^{-4} \text{m}^3)/(0.082 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1})(298 \text{ K})$$
$$= 0.041 \text{ mol}$$

At constant temperature, change of intropy $\triangle S$ is given

$$\triangle S = nR \ ln \frac{V_2}{V_1}$$

$$=(0.041)(8.31\ \text{JK}^{-1}\ \text{mol}^{-1})\ ln\left(\frac{1000\ \text{cm}^3}{500\ \text{cm}^3}\right)$$
$$=(0.34\ \text{JK}^{-1})\ ln\ 2$$
$$=0.24\ \text{JK}^{-1}.$$

8.10. ENTROPY OF MIXING FOR IDEAL GASES

When two or more gases are mixed together, there is an increase in entropy. It is possible to calculate entropy of mixing of gases, provided the gases are ideal.

Suppose n_1 moles of one gas at an initial pressure P_1° are mixed with n_2 moles of another gas at pressure P_2° under a constant temperature T. Let P_1 and P_2 be the partial pressures of the two gases in the mixture and P_t be the total pressure of the mixture, such that $P_t=P_1+P_2$.

By using equation (8.53), the entropies of the two gases in the mixture are given by

$$\triangle S_1=-n_1\ R\ ln\ \frac{P_1}{P_1^\circ}$$
$$=n_1\ R\ ln\ \frac{P_1^\circ}{P_1} \qquad \ldots (8.56a)$$

and

$$\triangle S_2=-n_2R\ ln\frac{P_2}{P_2^\circ}$$
$$=n_2R\ ln\frac{P_2^\circ}{P_2} \qquad \ldots (8.56b)$$

The total entropy of mixing is, then,

$$\triangle S_m=\triangle S_1+\triangle S_2=n_1R\ ln\ \frac{P_1^\circ}{P_1}+n_2\ R\ ln\ \frac{P_2^\circ}{P_2} \qquad \ldots (8.57)$$

But according to Dalton's Law of partial pressure, $P_1=X_1P_t$ and $P_2=X_2P_t$ where X_1 and X_2 are the mole fractions of the two gases. Substituting these identities in equation (8.57), we have

$$\triangle S_m=n_1\ R\ ln\ \frac{P_1^\circ}{X_1P_t}+n_2R\ ln\ \frac{P_2^\circ}{X_2P_t} \qquad \ldots (8.58)$$

If $P_1^\circ=P_2^\circ=P_t$, equation (8.58) becomes

$$\triangle S_m=-(n_1R\ ln\ X_1+n_2R\ ln\ X_2) \qquad \ldots (8.59)$$

Since X_1 and X_2 are less than unity, $\triangle S_m$ is always positive. Hence *the process of mixing is always accompanied by an increase in entropy.*

8.11. ENTROPY AND CHANGE OF STATE

The entropy of a system is determined by the freedom possessed by the molecules in the system. Solids have a low value for entropy since the molecules or atoms are tightly bound in an orderly fashion. The entropy increases when the solid melts to give liquid where the arrangement of atoms or molecules is less ordered. Similarly when a liquid is converted into vapor, the entropy will increase. Table 8.2 lists the values of boiling point, molar heat of vaporisation and entropy change per mole for some of the liquids.

TABLE 8.2

Liquid	*Boiling point (K)*	*Molar heat of vaporisation (cal)*	*Entropy change per mole (e.u.)*
Water	373	9700	26
Ethanol	351	9522	27
Methanol	338	8512	25
Ethyl bromide	311	5700	18
Ethyl Iodide	345	7322	21
Methyl Iodide	315	6532	21
Acetic acid	391	5664	15
Chloroform	334	6960	21
n-hexane	308	6500	21

It may be seen from this table that many liquids have a value of about 21 e.u. mole^{-1} which means that the increase in molecular chaos on going from liquid to vapor is nearly the same for these liquids. However, the higher values for water, ethanol and methanol indicate that these liquids, due to the presence of hydrogen bonding in them, have a high degree or order. The large entropy change comes because first this order is destroyed before the liquid is vaporised.

On the other hand, the entropy change upon melting of most solids lies in the range of 2 to 9 e.u. mole^{-1}. The larger increase in entropy of vaporisation indicates that the increase in disorder in going from a liquid to its vapors is larger than the change in going from a solid to its liquid.

To put the above discussion on a mathematical basis, consider the changes in entropy for a process involving a change of state such as fusion, vaporisation or sublimation. In each of these processes, the change in entropy is given by the heat required to accomplish the transition from one state to another divided by the absolute temperature at which the transition takes place. The only condition required is the existence of equilibrium between the two forms *i.e.*, transformation is a reversible process. The corresponding equations for the change in entropy in fusion, vaporisation and sublimation are given on next page.

$$\triangle S_f=\frac{\triangle H_f}{T_f}, \qquad \triangle S_v=\frac{\triangle H_v}{T_b}$$

and $$\triangle S_{sub}=\frac{\triangle H_{sub}}{T_{sub}}$$

where $\triangle H_f$, $\triangle H_v$, and $\triangle H_{sub}$ are the heats of fusion, vaporisation and sublimation respectively, and T_f, T_b and T_{sub} are the fusion, boiling and sublimation temperatures, respectively.

Since the entropy of vaporisation for most of the liquids at the normal boiling point is approximately equal to 21 e.u. per mole, this observation, called 'Trouton's Rule' can be employed to estimate an approximate value of the heat of vaporisation of a liquid if its boiling point (T_b) is known.

$$\triangle S_{vap}\approx 21 \text{ e.u.}$$

or $$\triangle H_{vap}\approx 21\ T_b$$

Problem 8.4. The molecular heat of vaporisation of water is 9717 cals mole^{-1} at 373.2 K. Determine the entropy change.

Solution. The entropy change is given by

$$\triangle S_v=\frac{\triangle H_v}{T_b}=\frac{9717}{373.2}$$
$$=26.04 \text{ e.u. mole}^{-1}.$$

If any process is irreversible, the equality $\triangle S=\frac{q}{T}$ does not hold. However in calculation for such processes, the use in made of the fact that since $\triangle S$ is a state function, only the initial and final states are important. Therefore, any irreversible process is carried out in a series of reversible steps in such a manner that the system reaches from the same initial stage to the final stage. The sum of the entropy changes for each of the reversible step will be the same as those for the entropy changes for the irreversible process.

Suppose it is desired to determine the entropy change for any irreversible, spontaneous process. As an example, consider the irreversible phase transition in which one mole of supercooled water freezes at −10°C and at one atm. pressure:

$$H_2O(l, -10°C) \dashrightarrow H_2O\ (S, -10°C)\ \triangle S=?$$

Since the given process is not a reversible one, its entropy change cannot be calculated directly. Here too, to calculate the entropy change, it is necessary to consider a series of reversible steps leading from the liquid water at −10°C to solid ice at −10°C. The various steps are:

(*i*) Heating very slowly (reversibly) 1 mole of supercooled water from −10°C to 0°C keeping the pressure constant.

(*ii*) Reversible conversion of a mole of water to a mole of ice at 0°C.

(*iii*) Cooling of a mole of ice very slowly (reversibly) from 0°C to −10°C.

Since each of these steps is reversible, the entropy changes can be calculated by the methods discussed earlier and their sum will be equal to entropy change for the irreversible process indicated above.

8.12. ENTROPY CHANGE IN CHEMICAL REACTIONS

Consider any chemical reaction represented by

$$lL+mM+\ldots=xX+yY+\ldots$$

The entropy change for such a reaction is given by

$$\triangle S=(xS_X+yS_Y+\ldots)-(lS_L+mS_M+\ldots) \quad \ldots (8.60)$$

where S_X, S_Y, etc., are the entropies per mole of the various species.

Entropy changes of chemical reactions are usually determined at constant temperature and pressure. The calculations are done as follows:

Differentiating equation (8.60) with respect to T at constant P we get

$$\left[\frac{\partial(\triangle S)}{\partial T}\right]_P=\left[x\left(\frac{\partial S_X}{\partial T}\right)_P+y\left(\frac{\partial S_Y}{\partial T}\right)_P+\ldots\right]$$
$$-\left[l\left(\frac{\partial S_L}{\partial T}\right)_P+m\left(\frac{\partial S_M}{\partial T}\right)_P+\ldots\right]$$

But, since $\left(\frac{\partial S}{\partial T}\right)_P=\frac{C_p}{T}$ (cf: equation 8.39*b*)

$$\text{Therefore, } \left[\frac{\partial(\triangle S)}{\partial T}\right]_P=\frac{(xC_{pX}+yC_{pY}+\ldots)}{T}-\frac{(mC_{pM}+nC_{pN}+\,.\,.)}{T}$$

$$=\frac{\triangle C_p}{T} \quad \ldots (8.61)$$

where $\triangle C_p$ is the difference between the $C_{p,s}$ of products and reactants.

Integrating equation (8.61) between the limits T_1 and T_2, we get

$$\int_{\triangle S_1}^{\triangle S_2} d(\triangle S)=\int_{T_1}^{T_2}\frac{\triangle C_p}{T}\,dT$$

or

$$\triangle S_2-\triangle S_1=\int_{T_1}^{T_2}\frac{\triangle C_p}{T}\,dT \quad \ldots (8.62)$$

Here, $\triangle S_2$ is the entropy change at T_2 and $\triangle S_1$ is the entropy change at T_1. If $\triangle C_p$ is constant, equation (8.62) becomes

$$\triangle S_2-\triangle S_1=\triangle C_p l_n\,\frac{T_2}{T_1} \quad \ldots (8.63)$$

But, if $\triangle C_p$ is not constant, then C_p has to be substituted as a function of T and the expression integrated between the limits T_1 and T_2.

8.13. STATISTICAL APPROACH TO ENTROPY

For a better appreciation of the concept of entropy it must be realised that a substance can have entropy due to factors other than the location in space of its particles. In addition to such translational entropy, it has entropy due to the distribution of energy between the available electron energy levels of its particles. This contribution to the total entropy is known as system's internal entropy. Consider an assembly of 36 atoms as shown in Fig. 8.6. If 36 quanta of energy are to be distributed among these atoms, three of the many possible ways this can be done are shown:

(*i*) One quantum is allotted to each atom; there is only one way this can be done, $W = 1$.

(*ii*) All the quanta can be given to one of the atoms, this can be done in 36 ways.

(*iii*) This is the most probable distribution if the quanta are allocated at random; there are 2×10^8 ways this can be done.

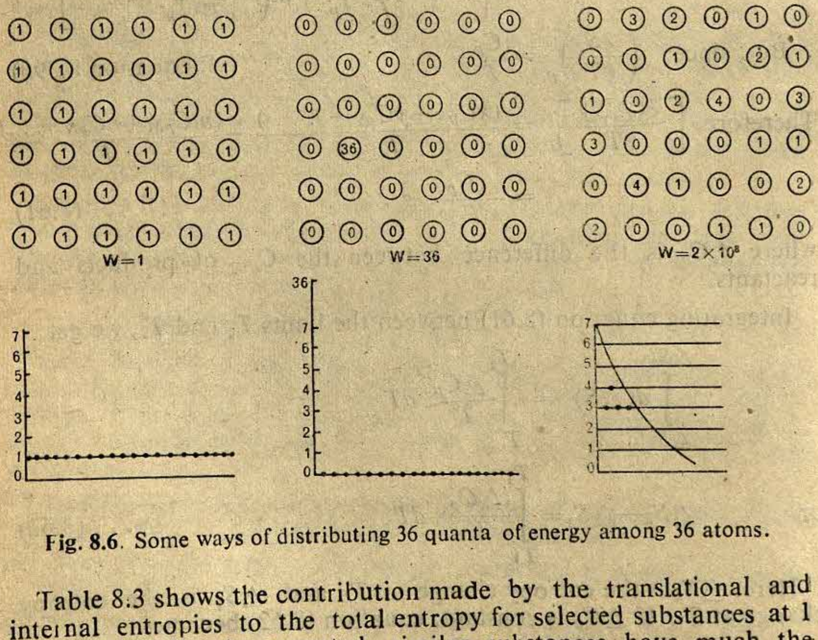


Fig. 8.6. Some ways of distributing 36 quanta of energy among 36 atoms.

Table 8.3 shows the contribution made by the translational and internal entropies to the total entropy for selected substances at 1 atm. and 298 K. As expected, similar substances have much the same values for translational entropy and the internal entropy increases sharply with molecular complexity because more electron energy levels are available.

TABLE 8.3.

Translational and internal entropies of some substances

Substance	*Entropy/J mol⁻¹ K⁻¹* *Translation*	*Internal*	*Total*
N_2O (g)	156	64	220
NO_2 (g)	157	83	240
N_2O_4	164	141	305

Boltzman proposed a logarithmic relationship between entropy and W, the ways the energy can be distributed (for internal entropy) or the ways the particles can be distributed in space (for translational entropy); the entropy per particle being

$$S=k\ ln\ W=\frac{R}{L}\ ln\ W$$

The Boltzmann constant, k is the gas constant per molecule.

Imagine two indentical flasks connected together by a stopcock. One flask is evacuated and the other contains 1 mole of gas. Let the total number of ways the translational energy can be distributed initially be W. If the stopcock is opened the gas will diffuse into the vacuum. W increases because each molecule now has twice the original volume in which to find itself.

The mole of gas consists of L molecules each having this choice of compartments, so the new number of ways of distributions is $2^L W$. The entropy change on expansion for each molecule can thus be calculated using Boltzmann's equation:

$$S_2-S_1=k ln 2^L\ W-k\ ln\ W$$
$$=k\ ln 2^L$$

Thus $\triangle S/\mathrm{J\ mol^{-1}}\ K^{-1}=R\ ln\ 2$

$$=5.77.$$

8.14. DETERMINATION OF ENTROPIES OF SUBSTANCES (THE THIRD LAW OF THERMODYNAMICS)

So far, the entropy difference but two states of a system could be calculated. Also, a molecular interpretation to the entropy has been given. When a system goes from an ordered state to a disordered state, the entropy is increased. The converse is also true. A perfectly ordered crystal at the absolute zero of temperature would then have a zero entropy value since the atoms in a crystal are perfectly ordered and confined to one position only. This gives rise to another universal empirical law, the third law of Thermodynamics, which states:

"*The entropy of a pure perfectly crystalline substance is zero at the absolute zero of temperature.*"

This statement is applicable only to pure crystalline solid substances because theoretical argument and experimental evidence have shown that the entropy of solutions and supercooled liquids is not zero at 0K. For perfectly crystalline substances, the law has been verified repeatedly and at present, there is no doubt about the general validity of the third law.

The third law finds considerable importance in the fact that it permits the calculation of absolute values of entropy of pure substances from thermal data alone. Let us briefly see how this is accomplished.

Consider a process involving the transformation of a solid from the absolute zero of temperature to some temperature T below its melting point:

$$\text{Solid } (0K, P) = \text{Solid } (T, P)$$

The entropy change for such a process is given by

$$\int_{S=S_O}^{S=S_T} dS = \int_{T=0}^{T=T} \frac{C_p}{T}\, dT$$

or

$$S_T - S_O = \int_0^T \frac{C_p}{T}\, dT$$

where S_T is the entropy at temperature T and S_O is the entropy at $0K$. Since by the third laws, $S_O=0$ at $T=0K$, one has

$$S_T = \int_0^T \frac{C_p}{T}\, dT = \int_0^T C_p\, dl_n T \qquad \ldots (8\ 64)$$

The integral in equation (8.64) is positive since the entropy can only increase with temperature. S_T, known as the absolute entropy of a substance or the third law entropy, is thus always a positive quantity and can be determined by integration of this equation if C_p of the solid is known from $T=0$ to the desired temperature.

Evaluation of absolute entropies. In order to determine the absolute entropy value of some chemical substance at temperature T, it is essential to evaluate the integral in equation (8 64). This integral is evaluated by determining the area under the curve between $T=0$ and any temperature T for the graph of $\frac{C_p}{T}$ versus T or for the graph of C_p versus l_nT. This area is then the value of the integral and hence of S_T. Since the heat capacity measurements cannot be made right down to the absolute zero, heat capacities are usually measured to as low temperature as possible *e.g.*, 10 to 15K and extrapolation is restored to from this range to $T=0$. Extrapolation is permissible because at such low temperature the heat capacity of solids follows the Debye "T—cubed" law accurately, namely

$$C_p=aT^3 \qquad \ldots (8.65)$$

where a is constant for each substance.

(Actually $C_v=aT^3$, but, since at extremely low temperature, the differences of C_p and C_v are negligible, so C_p values in the extrapolations of the curves can be used.)

A graph of C_p versus l_nT for anhydrous sodium sulphate is shown in Fig. 8.7. The area under the curve between $T=14$K and $T=298.2$K is 15.488, while the area between $T=0$ to $T=14$K is 0.026. The total area under the curve when multiplied by 2.303 yields absolute entropy per mole of sodium sulphate at 298.2K of 35.73 e.u.

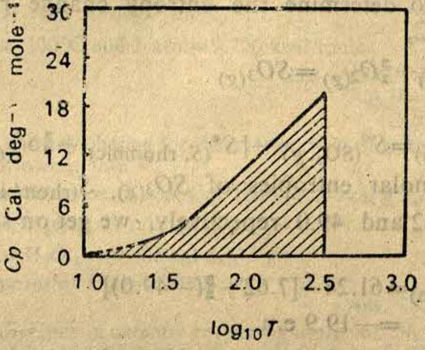


Fig. 8.7. Plot of C_p versus $\log_{10}T$.

Third law can also be utilised to determine absolute entropies of substances that are liquid or gaseous at ordinary temperatures. This is possible because we know that the total absolute entropy of a substance in a particular state at a given temperature is the sum of all the entropy changes the substance has to undergo in order to reach the particular state from the crystalline solid at 0K. Thus, to obtain the entropy of a gas above the boiling point of the substance, we should include (*a*) the entropy change of heating the crystalline solid from $T=0$ to $T=T_f$. the fusion point, (*b*) the entropy change on fusion, (*c*) the entropy change due to heating the liquid from the fusion temperature to boiling temperature T_b, (*d*) the entropy change due to vaporisation and (*e*) the entropy change due to heating of the gas from T_b to the desired temperature T. Equation (8.64) then becomes

$$S_T=\int_{0}^{T_f} C_{ps}\, d\ ln\ T+\frac{\triangle H_f}{T_f}+\int_{T_f}^{T_b} C_{p_l}\ d\ ln\ T+\frac{\triangle H_v}{T_b}+\int_{T_b}^{T} C_{p_g}\ d\ ln\ T \qquad \ldots (8.66)$$

If a substance is solid at temperature T, only the first integral is applicable with $T_f=T$; when it is liquid, the first three terms are utilised with $T_b=T$. When it is gaseous, the full equation is used. If the substance undergoes any transition between one crystalline modification, and another the entropy of transition at the equilibrium temperature must also be included in equation (8.66).

Absolute entropies may be used to calculate the entropy changes accompanying chemical reactions. The standard entropy change for a general chemical reaction is

$$\triangle S^\circ=\sum_i n_i S^\circ_{i(\text{products})}-\sum_i . S_{i(\text{reactants})} \qquad \ldots (8.67)$$

where n_i is the number of moles of component i in a balanced equation and S°_i is the standard molar entropy for component i. Thus in order to determine the entropy change required for the reaction at 25°C,

$$S_{(S,\ \text{rhombic})}+\tfrac{3}{2}O_{2(g)}=SO_{3(g)}$$

we have

$$\triangle S^\circ_{(\text{reaction})}=S^\circ_{(\text{SO}_3,\ g)}-[S^\circ_{(S,\ \text{rhombic})}+\tfrac{3}{2}S^\circ_{(O_2,\ g)}]$$

Since the molar entropies of $SO_{3(g)}$, $S_{(\text{rhombic},\ S)}$ and $O_{2(g)}$ are 61.24, 7.62 and 49.0 repectively, we get on substituting these values

$$\triangle S^\circ_{(\text{reaction})}=61.24-[7.62+\tfrac{3}{2}(-49.0)]$$
$$=-19.9 \text{ e.u.}$$

The Third Law of Thermodynamics lacks the generality of the other laws since it applies only to a special class of substances *i.e.*, pure, perfectly crystalline substances and not to all substances. Some substances, which are pure from the chemical standpoint, do not fulfil the requirement that the crystal be perfectly ordered at the absolute zero of temperature; they possess residual entropy. During recent years, remarkable progress has been made in the calculation of entropy and other thermodynamic properties from the methods based on quantum theory of energy and statistical mechanics. This branch of science is known as *Statistical Thermodynamics.*

PROBLEMS

1. Show that all reversible engines operating between the same two temperatures have the same efficiency.

What per cent T_1 is of T_2 for a 10 per cent efficiency of an heat engine?

Ans. $T_1=90\%$ of T_2

2. 1 gm of ice at 0°C is added to 10 g of H_2O at the boiling point. What will be the final temperature and the entropy changes accompanying the process? Assume that the heat of fusion of water is 80 cal/g and specific heat is 1 cal/g deg. **Ans.** $t=83.6°C$, $\triangle S=0.11$ e.u.

3. Efficiency of an irreversible engine is less than that of a reversible one. Explain this statement.

4. Clausius statement of the Second Law of Thermodynamics reads as follows:

> "It is impossible for an engine operating in a cycle to have as its only effect the transfer of a quantity of heat from a reservoir at low temperature to a reservoir at a higher temperature." Explain this statement.

5. Establish the following relationships:

(*a*) $$ds=\frac{C_p}{T}\,dT-V\alpha\,dP \quad [Hint\ S=f(T, P)]$$

(*b*) $$ds=\frac{C_v}{T}\,dT+\frac{\alpha}{\beta}\,dV \quad [Hint\ S=f(T, V)]$$

6. Calculate $\triangle S$, $\triangle H$ and $\triangle E$ for the process:

1 mole H_2O (liq, 20°C, 1 atm) → 1 mole H_2O (gas, 250°C, 1 atm) given the following data:

$\overline{C}_p$ (liq) = 18.0 cal deg^{-1} $mole^{-1}$

$\overline{C}_p$ (gas) = 8.6 cal deg^{-1} $mole^{-1}$

$\triangle\overline{H}_{vap}$ of H_2O at 100°C and 1 atm = 9.720 kcal/mole

Ans. $\triangle S=33.28$ cal deg^{-1} $mole^{-1}$
$\triangle H=12.450$ kcal/$mole^{-1}$
$\triangle E=11.410$ kcal/mole

7. Calculate the entropy change for the evaporation of water at 600 mm Hg pressure from the following data:

Latent heat of vaporisation of water at 100°C = 540 cal g^{-1},

$\overline{C}_p$ (50–100°C) for $H_2O_{(l)}=1.003$ cal deg^{-1} g^{-1}
for $H_2O_{(g)}=0.488$ cal deg^{-1} g^{-1}

Normal boiling point of H_2O = 100°C

Ans. 26.7 cal deg^{-1} $mole^{-1}$

8. What is the difference in entropy between 1 mole of N_2 at standard conditions and 1 mole of N_2 at 200°C when the molar volume is 50 litres?

Assume that $C_p=\left(\frac{7}{2}\right)R$ and N_2 behaves ideally.

Ans. $S=0.08$ e.u.

9. Using the relation:

$$ds=\left(\frac{C_p}{T}\right)dT-V\alpha\,dP$$

Show that

(*a*) $\left(\frac{\partial S}{\partial P}\right)_V=\beta C_p/T\alpha$

(*b*) $\left(\frac{\partial S}{\partial V}\right)_P=C_p/TV\alpha$

(*c*) $-\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_S=\beta/\gamma \quad (\gamma=C_p/C_p)$

10. For an adiabatic process, $q=0$ (by definition) and, therefore $\frac{q}{T}=\frac{0}{T}=0$. Why, then, is there an entropy increase ($\triangle S>0$) in an adiabatic expansion into a vacuum.

11. A quantity of an ideal gas in an isolated system is expanded isothermally and reversibly at 400 K from a volume V_1 to V_2. During the expansion, the gas absorbs 200 cals of heat from the reservoir in contact with it. Find (*a*) the entropy change of the gas, (*b*) the entropy change of the reservoir, and (*c*) the entropy change of the whole system.

Ans. (*a*) 0.50 e.u. (*b*)−0.50 e.u. (*c*) Zero

12. What is meant by Third Law Entropy. State the Third Law of Thermodynamics.

13. It is known that crystalline hydrogen has a residual entropy of 1.49 e.u. at the absolute zero of temperature. Can we say that this is in contradiction with the third law of thermodynamics ? Elaborate.

14. For a van der Waals gas show that:

(*a*) $$\left(\frac{\partial S}{\partial V}\right)_T=\frac{nR}{V-nb}$$

(*b*) $$\left(\frac{\partial S}{\partial P}\right)_T=\frac{V-nb}{\left(\frac{2na}{RTV^3}\right)(V-nb)^2-T}$$

(*c*) $$\left(\frac{\partial E}{\partial V}\right)_T=\frac{n^2a}{V^2}$$

(*d*) $$\left(\frac{\partial H}{\partial P}\right)_T=\frac{V-nb}{\left(\frac{2\,na}{RTV^3}\right)(V-nb)^2-1}+V$$

(*e*) $$\left(\frac{\partial E}{\partial P}\right)_T=\frac{(V-nb)^2}{\left(\frac{2}{V}\right)(V-nb)^2-\left(\frac{V^2RT}{na}\right)}$$

15. Comment on the following statements:

(*a*) Entropy of the universe is increasing.

(*b*) Death is natural and life abnormality.

(*c*) Entropy change at equilibrium is zero.

(*d*) 0K cannot be reached experimentally.

Chapter 9

FREE ENERGY FUNCTIONS

9.1. CRITERION OF EQUILIBRIUM

The second law of thermodynamics gives the condition of maximum entropy to define the position of equilibrium in systems at constant energy. This is a useful criterian for spontaneous chemical reactions.

Consider a system in contact with a reservoir at temperature T in which an infinitesimal irreversible process occurs and the only work done is the pressure-volume work. If q is the quantity of heat exchanged with the reservoir, then, since the process is irreversible, the entropy change ds for the system is greater than $\frac{q}{T}$ *i.e.*,

$$dS > \frac{q}{T} \qquad \ldots (9.1)$$

or

$$TdS > q$$

Since TdS is greater than q, $(q-TdS)$ is negative, *i.e.*, less than zero

$$q-TdS<0 \qquad \ldots (9.2)$$

Since the only work is the pressure-volume work,

$$q=dE+pdV$$

and equation (9.2) becomes

$$dE+pdV-TdS<0 \qquad \ldots (9.3)$$

This inequality is always applicable if a spontaneous change occurs and the only work involved is the pressure-volume work. If the volume and entropy of the system are held constant, then equation (9.3) reduces to

$$(dE)_{V,\,S}<0 \qquad \ldots (9.4)$$

Thus, for any irreversible process in a system of constant volume that does not change its entropy, the internal energy decreases. In other words, for a conservative mechanical system, the stable state is the one of lowest energy. A more careful statement of the role of the internal energy on position of equilibrium is that in systems of constant entropy, the equilibrium position is in the direction of lowest energy.

The volume and the internal energy of a system may be kept constant by isolating the system. For such a system, equation (9.3) becomes:

$$(-TdS)_{E,\,V}<0$$

which when multiplied by −1 and divided by T gives

$$(dS)_{V,\,E}>0 \qquad \ldots (9.5)$$

and so the entropy must increase in such an irreversible process. It can also be put in words that in systems of constant energy and constant volume, such as isolated systems, the equilibrium position is in the direction of highest entropy.

For the system which is not isolated, there are entropy changes in the adjacent systems which must also be considered. If the volume is constant during the infinitesimal irreversible process, equation (9.3) becomes:

$$(dE-TdS)_V<0 \qquad \ldots (9.6)$$

which can also be written as

$$d(E-TS)_{T,\,V}<0 \qquad \ldots (9.7)$$

The quantity $(E-TS)$ is referred to as the *Helmholtz free energy* and is represented by A,

$$A=E-TS \qquad \ldots (9.8)$$

Differentiating this equation at constant temperature

$$dA=dE-TdS \qquad \ldots (9.9)$$

and for a spontaneous process, equation (9.6) then becomes

$$(dA)_{T,\,V}<0 \qquad \ldots (9.10)$$

In other words, in an irreversible process at constant T and V, the Helmholtz free energy A decreases.

For a system at constant T and V, the PV work term will be zero. The system does no other work, therefore,

$$dA=0 \qquad \ldots (9.11)$$

Hence the condition of equilibrium for a system that can do no work is

$$dA=0.$$

To a chemist, the physical processes or chemical reactions which are of interest are usually carried out in the laboratory at constant temperature and pressure. For such processes, equation (9.3) can be written as:

$$d(E+PV-TS)_{T,\,P}<0 \qquad \ldots (9.3a)$$

The quantity $(E+PV-TS)$ is referred to as the *Gibb's free energy* and is represented by the symbol G, *i.e.*,

$$G=E+PV-TS \qquad \ldots (9.12)$$

or

$$G=H-TS \quad (\because H=E+PV)$$

For infinitesimal change under isothermal conditions, (*i.e.*, $dT=0$)

$$dG=dH-TdS \quad (\because SdT=0) \qquad \ldots (9.13)$$

This is an important relationship and can be put into words:

For a change at constant pressure and constant temperature and where only mechanical work is done, the free energy is equal to the *enthalpy change minus the product of the absolute temperature and the entropy change.*

Equation (9.3*a*) can be written as

$$(dG)_{T,\,P}<0 \qquad \ldots (9.14)$$

Thus in an irreversible process at constant T and P in which only pressure volume work is done, the Gibb's free energy decreases. Since both G and A are defined by an explicit equation in terms of variables which depend only upon the state of a system, both these are thermodynamic properties and their differentials are complete differential. Mathematically for a reversible cyclic process, we may write,

$$\oint dG=0 \qquad \ldots (9.15)$$

$$\oint dA=0 \qquad \ldots (9.16)$$

Table 9.1 summarises the conditions for reversibility and irreversibility for processes involving only pressure-volume work.

TABLE 9.1

Criteria for irreversibility and reversibility for processes involving only pressure-volume work

For irreversible processes	*For reversible process*
$(ds)_{V,\,E}>0$	$(dS)_{V,\,E}=0$
$(dE)_{V,\,S}<0$	$(dE)_{V,\,S}=0$
$(dA)_{T,\,V}<0$	$(dA)_{T,\,V}=0$
$(dG)_{T,\,P}<0$	$(dG)_{T,\,P}=0$

These relations may be applied to finite changes as well as to infinitesimal changes by replacing the *d's* by $\triangle$*'s*. It must however be remembered that spontaneous changes always go to the minimum (as in the case of Gibb's free energy at constant T and P) or to the maximum (as in the case of the entropy of an isolated system) and not to some other conditions even though the change to some other conditions satisfies the required inequality.

In this discussion, we have restricted ourselves only to those systems which involve pressure-volume work. If electrical work is done by the system, or if the temperature changes, the criteria for equilibrium will be altered. If a system is at constant T and P and does no additional work, the condition of equlibrium is $dG=0$. G will be at minimum when the system is at equilibrium as can be seen from Fig. 9.1.

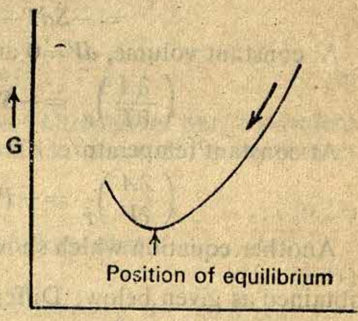


Fig. 9.1. Position of equilibrium in terms of Gibb's free energy for a system at constant temperature and pressure.

9.2. PROPERTIES OF HELMHOLTZ FREE ENERGY (A)

This function is defined as

$$A = E - TS$$

In order to understand the physical significance of A, consider the change in A when the system passes from state 1 to state 2, *i.e.*,

$$\begin{aligned}\triangle A &= A_2 - A_1\\ &= (E_2 - T_2 S_2) - (E_1 - T_1 S_1)\\ &= \triangle E - (T_2 S_2 - T_1 S_1)\end{aligned}$$

Under isothermal conditions, $T_2 = T_1 = T$, so that

$$\triangle A = \triangle E - T\triangle S \qquad \ldots (9.17)$$

Further, by definition of entropy, $\triangle S = \frac{q_r}{T}$

or $q_r = TdS$, so that we have

$$\triangle A = \triangle E - q_r \qquad \ldots (9.18)$$

But, since from first law of thermodynamics, for a reversible isothermal process, $\triangle E - q_r = -W_m$, we have

$$\triangle A = -W_m \qquad \ldots (9.19)$$

Hence at constant temperature, the maximum work obtainable from a system is at the expense of a decrease in the Helmholtz free energy of the system. This is why A is sometimes called the "work function" or the maximum work content of a system.

Further, if we completely differentiate the equation $A = E - TS$, we get

$$dA = dE - TdS - SdT \qquad \ldots (9.20)$$

But $TdS = q_r$ and $q_r = dE + PdV$, so that equation (9.20) becomes

$$\begin{aligned}dA &= dE - SdT - dE - PdV\\ &= -SdT - PdV\end{aligned} \qquad \ldots (9.21)$$

At constant volume, $dV = 0$ and

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \ldots (9.22)$$

At constant temperature, $dT = 0$ and

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \qquad \ldots (9.23)$$

Another equation which shows the variation of A with T can be obtained as given below: Differentiating the quantity $\frac{A}{T}$ with respect to T at constant V, we get

$$\left[\frac{\partial\left(\frac{A}{T}\right)}{\partial T}\right]_V = \frac{T\left(\frac{\partial A}{\partial T}\right)_V - A}{T^2}$$

$$=\frac{-(A+TS)}{T^2}$$

But $A+TS=E.$

Therefore, $$\left[\frac{\partial\left(\frac{A}{T}\right)}{\partial T}\right]_V=-\frac{E}{T^2} \qquad \ldots (9.24)$$

Isothermal change in work function. For an isothermal change, $dT=0$, and hence equation (9.21) yields

$$dA=-PdV$$

For one mole of a perfect gas, P may be replaced by $\frac{RT}{V}$, so that

$$dA=-RT\frac{dV}{V} \qquad \ldots (9.25)$$

For an appreciable process, the increase $\triangle A$ in the work function can be obtained by integration of equation (9.25) between the limits of the initial state 1 and final state 2; thus

$$\int_{A_1}^{A_2} dA=-\int_{V_1}^{V_2} RT\frac{dV}{V}$$

$$A_2-A_1=RT\ ln\ \frac{V_2}{V_1}$$

or $$\triangle A=RT\ ln\ \frac{V_1}{V_2} \qquad \ldots (9.26)$$

9.3. PROPERTIES OF GIBBS FREE ENERGY (G)

This function is defined by

$$G=E-TS+PV \qquad \ldots (9.27)$$

This definition may be written in two alternative but equivalent forms which are frequently employed. First, since H is equivalent to $E+PV$, hence

$$G=H-TS \qquad \ldots (9.28)$$

Second, since $A=E-TS$, it follows that

$$G=A+PV \qquad \ldots (9.29)$$

For a process taking place at constant pressure, the change in free energy is given by

$$\triangle G=\triangle A+P\triangle V \qquad \ldots (9.30)$$

If, in addition, the temperature in constant, $\triangle A=-W_m$ as seen from equation (9.19), so that equation (9.30) becomes

$$\triangle G=-(W_m-P\triangle V) \qquad \ldots (9.31)$$

The quantity W_m represents maximum work obtainable in the given change and includes all types of work such as electrical or surface work, in addition to work of expansion. The latter is equal to $P\triangle V$ and so W_m-PdV represents the reversible work, exclusive of work of expansion, that can be obtained from a given change in state. The quantity W_m-PdV is referred to as *network.*

Thus $-\triangle G=$network

The decrease in free energy at constant T and P is equal to the maximum network available for the given change in state which the process accompanies.

Again, from complete differential of equation (9.28) we get

$$dG=dH-TdS-SdT \quad \text{. . . (9.32)}$$

But $H=E+PV$, which on differentiation becomes

$dH=dE+PdV+VdP$. Also $TdS=dE+PdV$.

Making use of these identities into equation (9.32),

We get

$$dG=dE+PdV+VdP-dE-PdV-SdT$$

$$=-SdT+VdP \quad \text{. . . (9.33)}$$

At constant pressure, $dP=0$ and

$$\left(\frac{\partial G}{\partial T}\right)_P=-S \quad \text{. . . (9.34)}$$

At constant temperature, $dT=0$ and

$$\left(\frac{\partial G}{\partial P}\right)_T=V \quad \text{. . . (9.35)}$$

An alternate equation which shows the variation of G with T is obtained by differentiating the quantity G/T with respect to T at constant P, namely,

$$\left[\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right]_P=\frac{T\left(\frac{\partial G}{\partial T}\right)_P-G}{T^2}$$

$$=-\frac{(G+TS)}{T^2}$$

But $G+TS=H.$

Therefore, $$\left[\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right]_P=-\frac{H}{T^2} \quad \text{. . . (9.36)}$$

Isothermal changes in free energy function. At constant temperature, $dT=0$ and equation (9.33) becomes:

$$dG=VdP \quad \text{. . . (9.37)}$$

For 1 mole of a perfect gas, $PV=RT$

or $$V=\frac{RT}{P}$$

Substituting this into equation (9.37), we get

$$dG=\frac{RT}{P}dP \qquad \ldots (9.38)$$

Integrating between limits, equation (9.38) takes the form:

$$\int_{G_1}^{G_2} dG=RT\int_{P_1}^{P_2}\frac{dP}{P} \qquad \ldots (9.39)$$

$$G_2-G_1=RT\ ln\ \frac{P_2}{P_1} \qquad \ldots (9.40)$$

or $$\triangle G=RT\ ln\ \frac{P_2}{P_1} \qquad \ldots (9.41)$$

Generally, the free energy of a gas is related to the standard free energy G°. This is defined as the free energy of one mole of the gas at one atmosphere pressure. Equation (9.41) then becomes

$$G-G^\circ=RT\ ln\ \frac{P}{1}=RT\ ln\ P$$

or $$G=G^\circ+RT\ ln\ P \qquad \ldots (9.42)$$

9.4. THE GIBBS-HELMHOLTZ EQUATION

Since $$G=H-TS$$

Substituting the value of S from equation (9.34), we get

$$G=H+T\left(\frac{\partial G}{\partial T}\right)_P \qquad \ldots (9.43)$$

Similarly, substituting the value of S from equation (9.22) into equation $A=E-TS$, we get

$$A=E+T\left(\frac{\partial A}{\partial T}\right)_V \qquad \ldots (9.44)$$

These two equations are usually regarded as different forms of the Gibbs-Helmholtz equation. There are also other forms of the Gibbs-Helmholtz equation which are most widely used. They are deduced as shown below:

For a given reaction of the type,

$$\text{Reactants} \longrightarrow \text{Products}$$
$$\triangle G=G_p-G_r$$

where G_p is the sum total of the free energies of all the products and G_r is the sum total of the free energies of all the reactants.

From equation (9.28), we have

$G_p=H_p-TS_p$ and $G_r=H_r-TS_r$, so that by substitution

$$\begin{aligned}\Delta G&=(H_p-TS_p)-(H_r-TS_r)\\&=(H_p-H_r)-T(S_p-S_r)\end{aligned}$$

or $$\Delta G=\Delta H=T\Delta S \qquad \ldots(9.45)$$

where ΔS and ΔH are respectively the entropy and enthalpy change of the given isothermal reaction. Further, from equation (9.34)

$$-\Delta S=-(S_p-S_r)=\left(\frac{\partial G_p}{\partial T}\right)_P-\left(\frac{\partial G_r}{\partial T}\right)_P$$

or $$\left[\frac{\partial(G_p-G_r)}{\partial T}\right]_P=\left[\frac{\partial(\Delta G)}{\partial T}\right]_P \qquad \ldots(9.46)$$

Substituting this result into equation (9.45), we get

$$\Delta G=\Delta H+T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P \qquad \ldots(9.47)$$

Similarly, we can deduce the analogous expression

$$\Delta A=\Delta E+T\left[\frac{\partial(\Delta A)}{\partial T}\right]_V \qquad \ldots(9.48)$$

Equations (9.47) and (9.48) are alternate forms of the Gibbs-Helmholtz equation. These equations find numerous practical applications.

Still another form of the Gibbs-Helmholtz equation is obtained by differentiating $\frac{\Delta G}{T}$ with respect to T at constant P as given below:

$$\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_P=\frac{T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P-\Delta G}{T^2} \qquad \ldots(9.49)$$

But according to equation (9.47),

$$T\left[\frac{\partial(\Delta G}{\partial T}\right]_P=\Delta G-\Delta H$$

Therefore, equation (9.49) becomes

$$\begin{aligned}\left[\frac{\partial\frac{(\Delta G)}{T}}{\partial T}\right]_P&=\frac{\Delta G-\Delta H-\Delta G}{T^2}\\&=-\frac{\Delta H}{T^2} \qquad \ldots(9.50)\end{aligned}$$

Problem 9.1. One mole of a perfect gas at 27°C expands isothermally and reversibly from 10 atm to 1 atm against a pressure that is gradually reduced. Calculate q and W and each of the thermodynamic quantities, ΔE, ΔG, ΔH, ΔA and ΔS.

Solution. Since the process is carried out isothermally and reversibly from 10 atm to 1 atm against a pressure that is gradually reduced.

$$W_{max} = -RT \ln \frac{V_2}{V_1} = -2.303\ RT \log \frac{V_2}{V_1}$$

$$= -2.303\ RT \log \frac{P_1}{P_2}$$

$$= -(2.303 \times 8.314\ \mathrm{JK^{-1}\ mol^{-1}} \times 300.1\ \mathrm{K}) \log 10/1$$

$$= -5746\ \mathrm{J\ mol^{-1}}.$$

$$\Delta A = W_{max} = -5746\ \mathrm{J\ mol^{-1}}$$

Since the internal energy of a perfect gas is not affected by a change in volume,

$$\Delta E = 0.$$

$$q = \Delta E - W = 0 + 5746 = 5746\ \mathrm{J\ mol^{-1}}$$

$$\Delta H = \Delta E + \Delta(PV) = 0 + 0 = 0$$

Since PV is constant for a perfect gas at constant temperature

$$\Delta G = \int_{10}^{1} V dP = RT \ln \frac{1}{10} = 2.303\ RT \log \frac{1}{10}$$

$$= -2.303\ (8.314\ \mathrm{JK^{-1}\ mol^{-1}})\ (300.1\ \mathrm{K})$$

$$= -5746\ \mathrm{J\ mol^{-1}}$$

$$\Delta S = \frac{q_{rev}}{T} = \frac{5746\ \mathrm{J\ mol^{-1}}}{300.1\ \mathrm{K}} = 19.15\ \mathrm{JK^{-1}\ mol^{-1}}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{0 - (-5746\ \mathrm{J\ mol^{-1}})}{300.1\ \mathrm{K}}$$

$$19.15\ \mathrm{JK^{-1}\ mol^{-1}}.$$

9.5. MAXWELL RELATIONS

In the derivation of mathematical relationships between the different thermodynamic quantities, we shall concern ourselves only with the reversible processes involving pressure-volume work in closed systems in which there are no chemical reactions.

Since, from the second law of thermodynamics,

$$dS = \frac{q}{T} \qquad \ldots (a)$$

and from the first law, we have,

$$dE = q - PdV \qquad \ldots (b)$$

Combining the two equations, we get

$$dE = TdS - PdV$$

The differentials for H, G and V may be obtained from their definitions as shown below:

$$H=E+PV$$

$$dH=dE+PdV+VdP$$

or

$$=TdS+VdP$$

$$A=E-TS$$

$$dA=dE-TdS-SdT$$

or

$$=-SdT-PdV$$

$$G=H-TS$$

$$dG=dH-TdS-SdT$$

$$=dE+PdV+VdP-TdS-SdT$$

Introducing the expression for dE and simplifying, we get,

$$dG=-SdT+VdP$$

Thus, we have the following four analogous equations:

$$dE=TdS-PdV$$

$$dH=TdS+VdP$$

$$dA=-SdT-PdV$$

and

$$dG=-SdT+VdP$$

These four equations are sometimes called the four fundamental equations of thermodynamics. They may be compared with the mathematical expression for an exact differential as shown below:

$\because$ $$u=f(x,y)$$

$\therefore$ $$du=\left(\frac{\partial u}{\partial x}\right)_y dx+\left(\frac{\partial u}{\partial y}\right)_x dy$$

If du is an exact differential and is represented by

$$du=Mdx+Ndy$$

then their cross-derivatives are equal *i.e.*,

$$\left(\frac{\partial M}{\partial y}\right)_x=\left(\frac{\partial N}{\partial x}\right)_y$$

Application of this relation to the four fundamental equations yields the following four Maxwell relation :

$$\left(\frac{\partial T}{\partial V}\right)_S=-\left(\frac{\partial P}{\partial S}\right)_V \quad \ldots (9.51)$$

$$\left(\frac{\partial T}{\partial P}\right)_S=\left(\frac{\partial V}{\partial S}\right)_P \quad \ldots (9.52)$$

$$\left(\frac{\partial S}{\partial V}\right)_T=\left(\frac{\partial P}{\partial T}\right)_V \quad \ldots (9.53)$$

$$\left(\frac{\partial S}{\partial P}\right)_T=-\left(\frac{\partial V}{\partial T}\right)_P \quad \ldots (9.54)$$

These equations are very useful because they allow derivatives of thermodynamic functions to be expressed in other ways.

By using equations (9.53) and (9.54), it is possible to obtain another set of expressions for the entropy change (dS) in terms of experimentally measurable quantities. From the definitions of the coefficient of thermal expansion (α) and the coefficient of compressibility (β), we have

$$\alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \text{ and } \beta=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Applying the cyclic rule to the variables P, T and V, we have

$$\left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T=-1$$

Utilising the definitions of α and β, we get

$$\left(\frac{\partial P}{\partial T}\right)_V \cdot \frac{1}{V\alpha}\,(-V\beta)=-1$$

so that $$\left(\frac{\partial P}{\partial T}\right)_V=\alpha/\beta \qquad \ldots (9.55)$$

Using equation (9.55) in equation (9.53), we get

$$\left(\frac{\partial S}{\partial V}\right)_T=\alpha/\beta \qquad \ldots (9.56)$$

Again using the definition of α in equation (9.54), we obtain

$$\left(\frac{\partial S}{\partial P}\right)_T=-V\,\alpha \qquad \ldots (9.57)$$

The involved expressions (8.32) and (8.46) for dS obtained earlier in Chapter 8 can now be written in terms of simple expressions by using the relations (9.56) and (9.57). These are given below:

(*i*) When we write the total difference of entropy for any substance in terms of T and V, we have

$$dS=\left(\frac{\partial S}{\partial T}\right)_V dT+\left(\frac{\partial S}{\partial V}\right)_T dV$$

$$=\frac{C_p}{T}\,dT+V/\alpha\,dP \qquad \ldots (9.58)$$

(*ii*) In terms of T and P, entropy change is given by

$$dS=\left(\frac{\partial S}{\partial T}\right)_P dT+\left(\frac{\partial S}{\partial P}\right)_T dP$$

$$=\frac{Cp}{T}\,dT-V\,\alpha dP \qquad \ldots (9.59)$$

9.6. THERMODYNAMIC EQUATION OF STATE

From the second law of thermodynamics, we have the relation $dE=TdS-PdV$. For constant T, this equation can be written as

$$(\partial E)_T=T\,(\partial S)_T-P\,(\partial V)_T$$

Now dividing by $(\partial V)_T$, we have

$$\left(\frac{\partial E}{\partial V}\right)_T=T\left(\frac{\partial S}{\partial V}\right)_T-P$$

Substituting the value of $\left(\frac{\partial S}{\partial V}\right)_T$ from equation (9.53), we get

$$\left(\frac{\partial E}{\partial V}\right)_T=T\left(\frac{\partial P}{\partial T}\right)_T-P \qquad \ldots (9.60)$$

This equation is known as thermodynamic equation of state because it provides a relationship among P, V, T and the energy and is valid for all types of substances.

Similarly, restricting equation $dH=TdS+VdP$ to constant temperature and dividing by $(dP)_T$, we have

$$\left(\frac{\partial H}{\partial P}\right)_T=T\left(\frac{\partial S}{\partial P}\right)_T+V$$

Substituting the value of $\left(\frac{\partial S}{\partial P}\right)_T$ from equation (9.54), we get

$$\left(\frac{\partial H}{\partial P}\right)_T=-T\left(\frac{\partial V}{\partial T}\right)_P+V \qquad \ldots (9.61)$$

which is another thermodynamic equation of state expressing H in terms of P, V and T.

It is now possible, using equations (9.60) and (9.61), to prove the statement that for an ideal gas, the internal energy and enthalpy are functions of temperature only.

For such a gas,

$$P=\frac{nRT}{V}, \text{ so that at constant volumc}$$

$$\left(\frac{\partial P}{\partial T}\right)_V=\frac{nR}{V}$$

Substituting this value in equation (9.60), we see that

$$\left(\frac{\partial E}{\partial V}\right)_T=\frac{nRT}{V}-P$$

$$=P-P=O$$

Similarly, by substituting $\left(\frac{\partial V}{\partial T}\right)_P=\frac{nR}{P}$ in equation (9.61), we have

$$\left(\frac{\partial H}{\partial P}\right)_T = -\frac{nRT}{P}+V$$
$$=-V+V=0$$

This demonstration easily proves the validity of thermodynamic equation of state for an ideal gas.

With the help of equation (9.69), we can also get a simple expression for C_p-C_v. For this, we proceed as follows:

Substituting $\left(\frac{\partial P}{\partial T}\right)_V=\alpha/\beta$ from equation (9.55) in equation (9.60), we get

$$\left(\frac{\partial E}{\partial V}\right)_T=T\ \frac{\alpha}{\beta}-P=\frac{\alpha T-\beta P}{\beta} \qquad \ldots (9.62)$$

Since $$C_p-C_v=\left[\ P+\left(\frac{\partial E}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

or $$=\left[\ P+\left(\frac{\partial E}{\partial V}\right)_T\right]V\alpha$$

Substituting the value of $\left(\frac{\partial E}{\partial V}\right)_T$ from equation (9.62), we get

$$C_p-C_v=\left[\ P+T\ \alpha/\beta-P\right]V\alpha=\frac{TV\,\alpha^2}{\beta} \qquad \ldots (9.63)$$

This equation permits the evaluation of C_p-C_v in terms of quantities which are readily measurable for any substance.

9.7. CLAPEYRON EQUATION

The reationship between the variables in equilibrium between phases of one component systems, *e.g.*, liquid and vapor, solid and vapor, solid and liquid, etc., can also be obtained from a thermodynamic relationship, called Clapeyron equation.

Consider a liquid in equilibrium with its vapors at temperature T and pressure P. At equilibrium, let the temperature be changed to $T+dT$ and the pressure to $P+dP$, dT and dP being the infinitesimal changes in temperature and pressure respectively. Using the equation (9.33), we can write,

For liquid,

$$dG_{(l)}=V_{(l)}dP-S_{(l)}dT$$

and for vapors of the liquid,

$$dG_{(g)}=V_{(g)}dP-S_{(g)}dT$$

When the two phases are in equilibrium,

$$dG_{(l)}=dG_{(g)}$$

Equating the free energy changes,

$$V_{(l)}dP - S_{(l)}dT = V_{(g)}dP - S_{(g)}dT$$

and

$$\frac{dP}{dT} = \frac{S_{(g)} - S_{(l)}}{V_{(g)} - V_{(l)}}$$

or

$$\frac{dP}{dT} = \frac{\triangle S}{\triangle V} \qquad \ldots (9.64)$$

where $\triangle S$ and $\triangle V$ denote the changes of entropy and volume respectively.

Again at equilibrium, $\triangle G = 0$

$$\therefore \qquad \triangle G_{vap} = \triangle H_{vap} - T\triangle S_{vap} = 0$$

or

$$\triangle S_{vap} = \frac{\triangle H_{vap}}{T}$$

Substituting the value of $\triangle S_{vap}$ in equation (9.64) we get,

$$\frac{dP}{dT} = \frac{\triangle H_{vap}}{T\triangle V_{vap}} \qquad \ldots (9.65)$$

Equation (9.65) is known as Clapeyron equation and gives the rate of change of vapor pressure with temperature. The Clapeyron equation is a general equation and can be applied to any equilibrium between phases. Thus for sublimation and fusion processes, Clapeyron equation becomes

$$\frac{dP}{dT} = \frac{\triangle H_s}{T(V_g - V_s)}$$

and

$$\frac{dP}{dT} = \frac{\triangle H_f}{T(V_l - V_s)} \text{ respectively.}$$

9.8. CLAUSIUS-CLAPEYRON EQUATION

Clapeyron equation (9.65) can be put in a more convenient form applicable to vaporisation and sublimation equilibria in which one of the two phases is gaseous.

$$\triangle V_{vap} = V_{(g)} - V_{(l)}$$

Since the volume occupied by a liquid in a gaseous form is much large *i.e.*, $V_{(g)} >>>> V_{(l)}$, $V_{(l)}$ can be neglected in comparison to $V_{(g)}$.

$$\therefore \qquad \triangle V_{vap} = V_{(g)}$$

$$= \frac{RT}{P}$$

Substituting this in equation (9.65), we get

$$\frac{dP}{dT} = \frac{\triangle H_{vap} \times P}{RT^2}$$

or

$$\frac{dP}{P} = \frac{\triangle H_{vap}}{R}\,\frac{dT}{T^2} \qquad \ldots (9.66)$$

Integrating both sides of equation (9.66) between the limits P_1 and P_2 corresponding to the temperatures T_1 and T_2 we get,

$$\int_{P_1}^{P_2} \frac{dP}{P} = \frac{\triangle H_{vap}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

or
$$ln\ \frac{P_2}{P_1} = \frac{\triangle H_{vap}}{R} \left(\frac{T_2 - T_1}{T_2 T_1} \right) \qquad \ldots (9.67)$$

This is known as Clausius-Clapeyron equation. Despite of several approximations involved, equations (9.66) and (9.67) find numerous applications for the measurements of vapor pressure over various liquids and solids.

Problem 9.2. The vapor pressure of liquid A is 50 mm Hg at 46°C; this vapor pressure is 0.50 mm greater than that of solid A at the same temperature. At 45°C the vapor pressure of liquid is 1.00 mm Hg greater than that of the solid. $\triangle H_v$ is 9.0 kcal. (*a*) Estimate the melting point of A, (*b*) Calculate the heat of fusion of A, and its heat of sublimation.

Solution. (*a*) At the melting point, the liquid and solid must have the same vapor pressure. Since the difference is 1 mm at 45°C and 0.5 mm at 46°C, it should be zero at 47°C. Hence the melting point of solid should be 47°C. (*b*) The heat of fusion can be determined using the Clausius-Clapeyron equation. For the vapor at 46°C, we have:

$$\left[\frac{dP}{dT}\right]_v = \frac{\triangle H_v \times P}{RT^2}$$

$$= \frac{9000 \times 50}{1.98 \times (319)^2} = 2.2 \text{ mm/deg.}$$

Since the vapor pressure of the solid is increasing 0.5 mm/deg faster than that of the liquid.

Also
$$\left[\frac{dP}{dT}\right]_v = \frac{\triangle H_s \times P}{RT^2}$$

where $\triangle H_s$ is the heat of sublimation,

$$P = 50 + 2.7 = 52.7 \text{ mm}$$

$$2.7 = \frac{\triangle H_s \times 52.7}{1.98 \times 320 \times 320}$$

or
$$\triangle H_s = \frac{2.7 \times 1.98 \times 320 \times 320}{52.7}$$

$$= 10.35 \text{ kcal.}$$

The heat of fusion = Heat of sublimation − Heat of vaporisation

$$= \triangle H_s - \triangle H_v = 10.35 - 9.00$$

$$= 1.35 \text{ kcal.}$$

Problem 9.3. The boiling point of ether is 33.5°C at 760 mm pressure. At what temperature will it boil at a pressure of 750 mm. Given that the latent heat of vaporisation of ether is 88.4 calories per gram and has the molecular weight of 74.

Solution. The Clausius-Clapeyron equation is:

$$\log \frac{P_2}{P_1} = \frac{\triangle H_{vap} \times (T_2 - T_1)}{2.303 \times R \times T_1 T_2}$$

$$P_2 = 750 \text{ mm} \qquad T_2 = ?$$

Here $P_1 = 760$ mm $\quad T_1 = 306.5$ K

$\triangle H_{vap} = 88.4 \times 74$ calories per mole

$$\therefore \quad \log \frac{750}{760} = \frac{88.4 \times 74\,(T_2 - 306.5)}{2.303 \times 1.987 \times 306.5 \times T_2}$$

or

$$T_2 = 305.9 \text{ K}$$
$$= 32.9°\text{C}.$$

9.9. CHEMICAL POTENTIAL

In the discussion so far, we have considered thermodynamic systems containing only one chemical component. For studying the many component systems, particularly those which involve chemical reactions and transport of matter, it is necessary to add some terms to the equations for the closed systems.

For a pure substance or a system having the constant chemical composition, we have,

$$dG = VdP - SdT$$

In a many component system where the number of moles of various components of the system, n_1, n_2, . . . n_n, vary, further terms, may be added to the fundamental equation for the free energy. Thus for a many component system,

$$G = f(T, P, n_1, n_2, \ldots n_n)$$

and the total differential is

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,\,n_j} dT + \left(\frac{\partial G}{\partial P}\right)_{T,\,n_j} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,\,P,\,n_j} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,\,P,\,n_j} dn_2 + \ldots + \left(\frac{\partial G}{\partial n_n}\right)_{T,\,P,\,n_j} dn_n \quad \ldots (9.68)$$

where the subscript n_j indicates that the quantities of all components except the one in the derivative are kept constant.

If the system does not suffer any change in composition, then $dn_1 = 0$, $dn_2 = 0$ and so on and equation (9.68) reduces to

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,\,n_j} dT + \left(\frac{\partial G}{\partial P}\right)_{T,\,n_j} dP \quad \ldots (9.69a)$$

Comparison of this equation with equation, $dG = -SdT + VdP$, shows that

$$\left(\frac{\partial G}{\partial T}\right)_{P,\,n_j} = -S \ldots (9.69a) \text{ and } \left(\frac{\partial G}{\partial P}\right)_{T,\,n_j} = V \quad \ldots (9.69b)$$

In view of equations (9.69*a*) and (9.69*b*), the total differential of G in equation (9.68) becomes

$$dG = VdP - SdT + \left(\frac{\partial G}{\partial n_1}\right)_{T,\,P,\,n_j} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,\,P,\,n_j} dn_2 + \ldots + \left(\frac{\partial G}{\partial n_n}\right)_{T,\,P,\,n_j} dn_n \quad \ldots (9.70)$$

The coefficient of dn_1 in this equation is called the *chemical potential*, μ_1 of the 1 component. In general, chemical potential, μ_i, of the *i*th component is given by

$$\mu_i=\left(\frac{\partial G}{\partial n_i}\right)_{T,\,P,\,n_j} \qquad \ldots (9.71)$$

With this definition, equation (9.70) will take the form,

$$dG=VdP-SdT+\sum_i \mu_i\, dn_i \qquad \ldots (9.72)$$

where the sum includes all the constituents of the mixture.

Equation (9.72) is sometimes called the fundamental equation of chemical thermodynamics. From equation (9.71), the chemical potential of a substance *i* is equal to the rate of change in Gibb's free energy of the system with number of moles n_i of this component, when the number of moles of all other components are held constant. Chemical potential is an intensive property and may be regarded as a force which drives the chemical systems to equilibrium.

The fact that chemical potential of any substance in the system must have the same value throughout the system is an important equilibrium condition. There is always a spontaneous flow of matter from a region of high chemical potential to a region of low chemical potential just like spontaneous flow of water from a high level to a low level or spontaneous flow of electric current from a region of high chemical potential to a region of low chemical potential. Chemical potential may also be referred to as the escaping tendency of that substance. Higher the chemical potential of a substance in a system, greater will be escaping tendency of that substance and *vice versa*.

9.10. THE GIBBS-DUHEM EQUATION

Since
$$dG=VdP-SdT+\sum_i \mu_i\, dn_i$$

At constant temperature and pressure, this becomes

$$dG=\sum_i \mu_i\, dn_i$$

By integrating this equation, we have

$$G=\sum \mu_i\, n_i \qquad \ldots (9.73)$$

Differentiating equation (9.73), we obtain

$$dG=\sum (n_i\, d\mu_i+\mu_i\, dn_i) \qquad \ldots (9.74)$$

Subtracting equation (9.74) from equation (9.72), we get

$$\sum n_i \, d\mu_i = VdP - SdT \qquad \ldots (9.75)$$

This is known as the Gibbs-Duhem equation.

At constant temperature and pressure, if the only variation in composition takes place, equation (9·75) takes the form

$$\sum n_i d\mu_i = 0 \qquad (T,\ P \text{ constant}) \qquad \ldots (9.76)$$

This equation shows that with variations in compositions, the chemical potentials do not change independently but in a related way. Consider, for example, a system of two constituents of compositions n_1 and n_2 respectively. For such a system, equation (9.76) becomes

$$n_1 \, d\mu_1 + n_2 \, d\mu_2 = 0 \qquad (T,\ P \text{ constant})$$

or

$$d\mu_2 = -\left(\frac{n_1}{n_2}\right) d\mu_1 \qquad \ldots (9.77)$$

With the help of this equation it is possible to find the change in the chemical potential $d\mu_2$ of the second constituent by knowing a change in the chemical potential $d\mu_1$ of the first constituent that results due to the variation in composition. Table 9.2 gives various thermodynamic quantities.

TABLE 9.2

Various Thermodynamic Functions

Definition	*Function*	*Name*
$dE = dq + dw$	E	Internal Energy
$dS = \frac{dq_{rev}}{T}$	S	Entropy
$H = E + PV$	H	Enthalpy
$G = H - TS$	G	Gibbs free Energy
$A = E - TS$	A	Helmholtz free energy (work function)
$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,\ P,\ n_j}$	μ_i	Chemical potential
$C_p = \left(\frac{\partial H}{\partial T}\right)_P$	C_P	Heat capacity at constant pressure
$C_v = \left(\frac{\partial E}{\partial T}\right)_V$	C_V	Heat capacity at constant volume

9.11. APPLICATIONS OF CHEMICAL POTENTIAL

In this section we shall briefly discuss some of the applications of chemical potential in the study of chemical phenomena.

(*a*) *Chemical potential of pure substances.* The chemical potential for a pure substance is given by

$$\mu_i=\left(\frac{\partial G}{\partial n_i}\right)_{T,\,P,\,n_j}=\bar{G}_i \qquad \ldots (9.78)$$

where $\bar{G}_i$ is defined as the partial molar free energy of component i in the system. The other partial molar quantities are defined as:

$$\left(\frac{\partial V}{\partial n_i}\right)=\bar{V}_i \qquad \ldots (9.79)$$

$$\left(\frac{\partial S}{\partial n_i}\right)=\bar{S}_i \qquad \ldots (9.80)$$

where $\bar{V}_i$ and $\bar{S}_i$ are the partial molar volume and partial molar entropy. From relation $dG=VdP-SdT$, we have

$$\left(\frac{\partial G}{\partial P}\right)_T=V$$

On substituting the value of V in (9.79), we get

$$\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial P}\right)_T=\bar{V}_i$$

or

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T=\bar{V}_i \qquad \ldots (9.81)$$

A similar argument gives

$$\left(\frac{\partial \mu_i}{\partial T}\right)_P=-\bar{S}_i \qquad \ldots (9.82)$$

Partial molar qauntities play an important role in the study of non-ideal mixtures. With the help of equation (9.81), one can calculate the chemical potential of the gases, liquids and solids, provided the pressure dependence of volume is known.

(*b*) *The study of phase equilibria.* Consider a substance *i* distributed between two phases α and β as shown in Fig. 9.2.

Let μ_i (α) and μ_i (β) be the chemical potential of the substance in the two phases and dn_i be the number of moles of *i* transferred from phase α to the phase β at constant temperature and pressure. Using equation (9.72), we get:

$$dG=[\mu_i(\beta)-\mu_i(\alpha)]\,dn_i.$$

At equilibrium, $dG=0$ and for a small finite change in the number of moles of *i*, dn_i will be non-zero. Thus

$$\mu_i(\beta)-\mu_i(\alpha)=0$$

or

$$\mu_i(\alpha)=\mu_i(\beta)$$

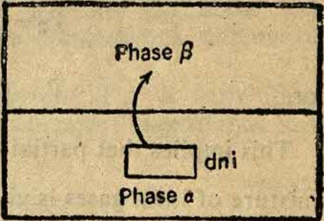


Fig. 9.2. A component *i* being distributed between two phases α and β.

Hence at equilibrium, at constant temperature and pressure, the chemical potential of each component must be equal in all parts of the system.

(*c*) *Chemical potential for an ideal gas.* From equation (9.42), the free energy of one mole of an ideal gas at one atmospheric pressure is given by

$$G=G^{\circ}+RT\ ln\ P$$

If there are n moles of the gas, the above equation takes the form

$$G=G^{\circ}+n\ RT\ ln\ P$$

or
$$\frac{G}{n}=\frac{G^{\circ}}{n}+RT\ ln\ P$$

But
$$\mu=\frac{G}{n}$$

Therefore, the molar free energy or the chemical potential of an ideal gas is given by

$$\mu=\mu^{\circ}+RT\ ln\ P \qquad \ldots (9.83)$$

(*d*) *Chemical potential in an ideal gas mixture.* Suppose there is a system containing $(n_1+n_2+n_3+\ldots)$ moles of various ideal gases at any constant temperature T. Let p_1, p_2, $p_3 \ldots$ be the partial pressures of gases in mixture. For such a system, we have

$$n=n_1+n_2+n_3+\ \ldots$$
$$p=p_1+p_2+p_3+\ \ldots$$

and
$$V=(n_1+n_2+n_3+\ \ldots)\ \frac{RT}{P}$$

Differentiating the volume (V) with respect to number of moles of any component, keeping T, P and number of moles of all other gases constant, we find

$$\bar{V}_1=\left(\frac{\partial V}{\partial n_1}\right)_{T,\ P,\ n_j}=\frac{RT}{P}$$
$$\bar{V}_2=\left(\frac{\partial V}{\partial n_2}\right)_{T,\ P,\ n_j}=\frac{RT}{P}$$

or
$$\bar{V}_i=\left(\frac{\partial V}{\partial n_i}\right)_{T,\ P,\ n_j}=\frac{RT}{P}$$

This implies that partial molar volume of any component in a mixture of ideal gases is given by $\frac{RT}{P}$. Thus equation (9.81) becomes

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,\ n_j}=\frac{RT}{P}$$

or
$$d\mu_i=RT\frac{dP}{P}=RT\ dln\ P$$

But the partial pressure of the component i is given by

$$p_i = \frac{n_i}{n} P$$

For the given system, as n_i and n are constant, $d \ln p_i = d \ln P$, so that

$$d\mu_i = RT\, d\, ln\, p_i$$

Integrating this equation, we have

$$\mu_i = \mu^\circ_i + RT\, ln\, p_i \qquad \ldots (9.84)$$

where μ°_i is the integration constant.

This equation suggests that the chemical potential of any component in a mixture of ideal gases can be calculated from its partial pressure in the mixture.

Equation (9.84) can also be written in the following alternate forms:

(*i*) Since $p_i = C_i\, RT$ where C_i=concentration per mole of component i.

Then

$$\mu_i = \mu_i + RT\, ln\, RT + RT\, ln\, C_i$$

$$= \mu^\circ_{i(c)} + KT\, ln\, C_i \qquad \ldots (9.85)$$

where

$$\mu^\circ_{i(c)} = \mu^\circ_i + RT\, ln\, RT$$

(*ii*) Again, from Dalton's law of partial pressure in terms of mole fraction, we have $p_i = PX_i$

where X_i is the mole fraction of component i and P is the total pressure. Therefore, equation (9.84) is written as

$$\mu_i = (\mu^\circ_i + RT\, ln\, P) + RT\, ln\, X_i$$

$$= \mu_{i(\text{pure})} + RT\, ln\, X_i \qquad \ldots (9.86)$$

where $\mu_{i(\text{pure})} = \mu_i + RT\, ln\, P$ is the chemical potential for pure i under the pressure P.

Since $X_i < 1$ and its logarithm is negative, it follows from equation (9.86) that the chemical potential of any gas in a mixture is always less than the chemical potential of the pure gas under the same total pressure. This explains for the spontaneous mixing of gases into each other.

Similar considerations apply to solutions also. For a truly ideal solution, the relevant equation for the chemical potential of any component i in the solution is

$$\mu_{i(\text{sol}^n)} = \mu^\circ_i\, (l) + RT\, ln\, X_i \qquad \ldots (9.87)$$

where $\mu^\circ_i\, (l)$ is the chemical potential of the pure liquid and X_i is the mole fraction of the component i in the solution.

(*e*) *Chemical potential of real gases and fugacity*. Equation (9.83) for chemical potential,

$$\mu = \mu^\circ + RT\, ln\, P$$

is applicable only to ideal gases.

For real gases, Lewis (1901) introduced a new function, called the *fugacity* f, and defined it by an equation analogous to equation (9.83). Thus, the chemical potential of a pure real gas is expressed as

$$\mu=\mu^\circ+RT\ ln\ f \qquad \ldots(9.88)$$

The fugacity is regarded as a sort of idealized partial pressure and includes in it all the effects arising due to imperfections of the real gases. For an ideal gas, the fugacity becomes equal to the pressure. Since, however, any real gas tends to behave ideally when its pressure is reduced to zero, we can complete the definition of the fugacity of any gas by stating, that in general,

$$f=P \text{ as } P\rightarrow 0 \qquad \ldots(9.89a)$$

$$\text{or that } \lim_{P\rightarrow 0} f/P=1 \qquad \ldots(9.89b)$$

The ratio f/P is called the fugacity coefficient of a gas and is denoted by γ. It is a measure of the extent to which any real gas deviates from ideal behaviour at any given temperature and pressure.

In a mixture of real gases, the chemical potential of any constituent i is given by

$$\mu_i=\mu^\circ_i+RT\ ln\ \frac{f_i}{f_i^\circ}$$

The ratio of the fugacity f_i to the fugacity in a standard state, f_i° is called the activity a_i

$$a_i=\frac{f_i}{f_i^\circ} \qquad \ldots(9.90)$$

In terms of activity, chemical potential is expressed as

$$\mu_i=\mu^\circ_i+RT\ ln\ a_i \qquad \ldots(9.91)$$

9.12. ACTIVITIES AND ACTIVITY COEFFICIENTS

In order to describe correctly the properties and behaviour of a non-ideal mixture or solution the 'strength', *i.e.* the mole fraction, molality, concentration or partial pressure of each substance must be replaced by the activity of the substance in the appropriate formulae. The correction factor which is used to correct the 'strength' so as to give the activity is known as the activity coefficient, *i.e.*

activity=activity coefficient × 'strength'

The quantities and units by which the 'strength' of a given mixture or solution is speicfied, *e.g.* mole fraction, molality, concentration or partial pressure will affect the activity coefficent but not the activity. The activity of a substance in mixture or solutions depends on the amount of substance present and on the standard state chosen to correspond to unit activity.

For solvents of solutions and for components of liquid, solid or gaseous mixtures in which no distinction is made between solvent and solute, the standard state is taken to be the pure substance for which the mole fraction is also unity. In this case, we have

activity = activity coefficient × mole fraction

which for substance *B* may be stated symbolically

$$a_B = f_B \times x_B \qquad \ldots (9.92)$$

As the solution becomes richer and richer in component *B*, which may be the solvent such as water, $x_B \rightarrow 1.0, a_B \rightarrow 1.0$, therefore $f_B \rightarrow 1.0$. For ideal solutions at all concentrations, $a_B = x_B$, therefore, $f_B = 1.0$. For solutions exhibiting positive deviations from Raoult's law $a_B > x_B$, therefore $f_B > 1$ and for solutions showing negative deviations, $a_B < x_B$, therefore $f_B < 1$, provided that $x_B \neq 1$.

In the case of solutes in solution, such as drugs and electrolytes dissolved in water, the activity coefficient is taken to be unity for an infinitely dilute solution, *i.e.*

activity = 'molal' activity coefficient × molality

$$a_B = \gamma_B \times m_B \qquad \ldots (9.93)$$

a_B = 'molar' activity coefficient × concentration

$$a_B = y_B \times c_B \qquad \ldots (9.94)$$

For a given solution the activity, a_B, is the same using any one of these equations, but the activity coefficients are generally different. The standard state of the solute in a solution is such that it has unit activity. Since very dilute solutions behave almost ideally, a approaches m (or c) and therefore γ (or y) approaches unity for such solutions. Table 9.3 gives variation of activity coefficient for an electrolyte and non-electrolyte with dilution.

TABLE 9.3.

Variation of activity coefficent with molality in water

$m/(mol\ kg^{-1})$	γ *for NaCl*	γ *for glycerol*
0	1.00	1.00
0.005	0.930	—
0.1	0.778	1.006
0.5	0.679	1.032
1.0	0.656	1.068
2.0	0.670	1.132
3.0	0.719	—
5.0	—	1.348

PROBLEMS

1. Derive the conditions for thermodynamic equilibrium and spontaneity in a system of constant composition.

2. Why in the use of entropy, as a criterion for spontaneity, do we have to consider $\Delta S_{\text{universe}} = \Delta S_{\text{system}} - \Delta S_{\text{surroundings}}$, but in case of the Gibbs free energy we have to consider only ΔG_{system} (not $\Delta G_{\text{universe}} = \Delta G_{\text{system}} - \Delta G_{\text{surroundings}}$).

3. The values of ΔH and ΔS for a chemical reaction are -22.6 kcal and -45.2 cal/deg respectively and these values are not very much affected by temperature changes.

(*a*) Calculate ΔG for the reaction at 3000 K.

(*b*) Calculate ΔG for the reaction at 1000 K.

Ans. (*a*) $-9{,}040$ cal (*b*) $+22{,}600$ cal.

4. Calculate ΔH, ΔS and ΔG when 1 mole of water is converted from liquid at 100°C and 1 atm pressure to vapor at the same temperature and pressure. Discuss the influence of the entropy and energy factors on the spontaneity of the reaction.

5. The vapor pressure of acetonitrile is changing at the rate of 0.03 atm/deg near its normal boiling point which is 18°C. Calculate the heat of vaporisation.

Ans. 7.4 kcal/mole.

6. For a certain substance, the change in entropy on melting is 3 cal/deg per c.c. of solid which melts. The melting point under 1 atm pressure is 6°C and densities of the solid and liquid are 0.90 and 0.85 g/c.c. respectively. Calculate the melting point under 10^4 atm pressure.

Ans. 4.9°C.

7. Calculate the change in entropy for the isothermal compression of 50 g of oxygen at 300 K from 5 atm to 25 atm using (*a*) the ideal gas law, (*b*) the van der Waals equation.

Ans. (*a*) -5.00 e.u.; (*b*) -5.15 e.u.

8. Show that

(*a*) $dH = TdS + VdP$

(*b*) $dE = TdS - PdV$

(*c*) $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

9. Explain the term chemical potential. Give a brief account of its applications.

10. Write notes on the following:

(*a*) Clausius-Clapeyron equation

(*b*) Gibbs-Helmholtz equation

(*c*) Gibbs-Duhem equation

(*d*) Partial Molal quantities.

11. Determine the change in free energy for the conversion of two moles of benzene liquid to vapor at 1 atm pressure (*a*) at the b.p. 80.1°C, (*b*) at 40°C, The vapor pressure of benzene at 40°C is 182.7 mm.

Ans. (*a*) 0; (*b*) 1775 cal.

Chapter 10

CHEMICAL EQUILIBRIUM

10.1. REVERSIBLE PROCESSES

We know from experience that all chemical reactions are reversible, *i.e.*, they proceed in both directions. Consider, for example, a simple reaction of the type

$$A+B\rightleftharpoons C+D$$

(double arrows indicate that the reaction is reversible).

Here, A and B are two reactants which react to give the products, C and D. If the products are not allowed to escape, then as soon as they accumulate, they react to reform the reactants. C and D react under the same conditions at which A and B react so that a stage is reached at which A and B react to give as much C and D as C and D react to give A and B. In other words, the rate of the forward reaction becomes equal to the rate of the backward reaction and thus a reaction never goes to completion. When a reaction reaches this stage, it is said to be in a stage of *chemical equilibrium*, a state at which the compositions of the reactants and products get fixed. At chemical equilibrium, no perceptible transformation can be observed in the system and the reaction appears to come to standstill although in reality, the forward and backward reactions are proceeding at equal speeds all the time. Thus chemical equilibrium is *dynamic* in nature.

Under any given conditions of pressure and temperature, the point at which equilibrium is established between the reactants and products is always the same although we may proceed from either direction for a given reversible reaction. This can be illustrated by considering the reaction between H_2 and I_2 in a closed vessel which may be represented as:

$$H_2+I_2\rightleftharpoons 2HI$$

At a temperature of 425°C, the composition of the equilibrium mixture is found to be 12 per cent of H_2, 12 per cent of I_2 and 76 per cent of HI. If the reaction is started with HI at the same temperature, we shall find that the same composition persists for the equilibrium mixture.

10.2. THE LAW OF MASS ACTION

This law helps us to find the relations among the concentrations of reactants and products at equilibrium in chemical reactions and was first enunciated by Guldberg and Waage in 1864. *This law states that at constant temperature, the rate at which a substance reacts is directly proportional to its "active mass." The velocity of a chemical reaction is proportional to the products of the 'active masses' of the reactants.*

The ambiguous term "active mass" in the above statement is a thermodynamic quantity and is given by $a=c.\ f$, where a is the active mass, c is the molecular concentration and f is its activity coefficient. For reactions involving gases and solutions, $f=1$ and "concentration" may be substituted for "active mass".

Consider a general reversible reaction

$$A+B \rightleftharpoons C+D \qquad \ldots (10.1)$$

According to the law of mass action, the rate of the forward reaction, R_f, at any time is proportional to C_A and C_B, the concentrations of A and B respectively and is given by

$$R_f=k_1\, C_A\, C_B \qquad \ldots (10.2)$$

where k_1 is a proportionality constant for the forward reaction. Similarly, the rate of the reverse reaction, R_r, is given by

$$R_r=k_2 C_C C_D \qquad \ldots (10.3)$$

where k_2 is the proportionality constant for the reverse reaction and C_C and C_D stand for the concentrations of C and D respectively.

At equilibrium, the two rates must be equal. Hence,

$$R_f=R_r$$

or

$$k_1 C_A C_B=k_2 C_C C_D$$

By rearranging this equation, we get

$$\frac{C_C C_D}{C_A C_B}=\frac{k_1}{k_2}=K_c \qquad \ldots (10.4)$$

The constant K_c is known as the *equilibrium constant* of the particular reaction and gives the ratio of the product of concentrations of resultants to the product of the concentrations of the reactants. The subscript c indicates that the equilibrium condition is expressed in terms of the concentration units, *i.e.*, moles per litre of the various species.

If we consider a process involving more than a single molecule of each of the reactants and products, then *the rate is proportional to the concentration of the given substance raised to a power equal to the number of molecules of the substance participating*. Thus, for the reaction

$$\alpha A+bB+\ldots \rightleftharpoons cC+dD+\ldots \qquad \ldots (10.5)$$

the two rates are given by

$$R_f=k_1\, C_A^{\alpha} C_B^{b} \qquad \ldots (10.6)$$

and

$$R_r=k_2\, C_C^{c}\, C_D^{d} \qquad \ldots (10.7)$$

and the expression for the equilibrium constant in terms of concentration is

$$\frac{C_C^c\ C_D^d}{C_A^\alpha\ C_B^b}=\frac{k_1}{k_2}=K_c \qquad \ldots (10.8)$$

Equation (10.8) gives the most general definition of the equilibrium constant. By convention, the equilibrium concentrations of the substances appearing on the right hand side of the chemical equation (the products) are always placed in the numerator of the equilibrium constant expression and the concentrations of the substances appearing on the left hand side of the chemical equation (the reactants) are placed in the denominator. It should be borne in mind that the reciprocal of K_c as defined by equation (10.8) will also be constant and the two constants are related to each other by the expression given below:

$$K_{direct\ action}=\frac{1}{K_{reverse\ reaction}} \qquad \ldots (10.9)$$

10.3. THERMODYNAMIC DERIVATION OF THE EQUILIBRIUM CONSTANT

Consider the general reaction

$$\alpha A+bB+\ldots\rightleftharpoons cC+dD+\ldots \qquad \ldots (10.10)$$

We know that the chemical potential of a substance in the mixture is related to its activity by means of the equation

$$\mu=\mu^\circ+RT\ ln\ a \qquad \ldots (10.11)$$

where μ° is the chemical potential of the pure substance in the standard state of unit activity.

Again, for the given reaction,

$$\text{free energy of the products}=c\mu_C+d\mu_D+\ldots \qquad \ldots (10.12)$$

$$\text{and free energy of the reactants}=\alpha\mu_A+b\mu_B+\ldots \qquad \ldots (10.13)$$

where μ terms stand for the chemical potential of various substances. If the values of chemical potential as defined by equation (10.11), are substituted in equations (10.12) and (10.13), the difference in free energy, $\triangle G$ is given by

$$\begin{aligned}\triangle G=&[c(\mu^\circ{}_C+RT\ ln\ a_C)+d(\mu^\circ{}_D+RT\ ln\ a_D)]\\ &-[\alpha(\mu^\circ{}_A+RT\ ln\ a_A)+b(\mu^\circ{}_B+RT\ ln\ a_B)]\end{aligned} \qquad \ldots (10.14)$$

where a_A and a_B are the activities of A and B (reactants) and a_C and a_D are the activities of C and D (products).

On rearrangement of equation (10.14), we get

$$\triangle G=\triangle G^\circ+RT\ ln\left(\frac{a_C^c.a_D^d\ldots}{a_A^\alpha.a_B^b\ldots}\right) \qquad \ldots (10.15)$$

where $\triangle G^\circ$ stands for the difference in free energy of the reaction when all the reactants and products are in their respective standard states and is given by

$$\triangle G^\circ = (c\mu^\circ_C + d\mu^\circ_D + \ldots) - (\alpha\mu^\circ_A + b\mu^\circ_B + \ldots) \quad \ldots (10.16)$$

It should also be kept in mind that in equation (10.15), all the activities indicated are those of the products at the end and of the reactants at the start of the reaction.

Again, at equilibrium, $\triangle G = 0$, provided the pressure and temperature are constant. Therefore, at equilibrium, equation (10.15) becomes

$$0 = \triangle G^\circ + RT\, ln \left(\frac{a_C^c . a_D^d \ldots}{a_A^\alpha . a_B^b \ldots} \right)_e$$

or

$$\triangle G^\circ = -RT\, ln \left(\frac{a_C^c . a_D^d \ldots}{a_A^\alpha . a_B^b \ldots} \right)_e \quad \ldots (10.17)$$

The subscript e indicates that the activities are those of reactants and products at equilibrium. Since at any given temperature the standard free energy change $\triangle G^\circ$ is a constant for any given reaction, it follows that the right hand side of equation (10.17) must also be constant *i.e.*,

$$\left(\frac{a_C^c . a_D^d \ldots}{a_A^\alpha . a_B^b \ldots} \right)_e = \text{Constant} = K_a \quad \ldots (10.18)$$

where K_a is the thermodynamic equilibrium constant of a reaction. K_a is constant only at a particular temperature. If temperature changes, it will also change. Thus equation (10.17) becomes

$$\triangle G^\circ = -RT\, ln\, K_a \quad \ldots (10.19)$$

Knowing K_a, it is possible to calculate $\triangle G^\circ$ at a given temperature.

10.4. EQUILIBRIUM CONSTANTS EXPRESSED IN DIFFERENT UNITS

For reactions involving gases, it is convenient to express concentration of any gas at any given temperature in terms of its partial pressure. To define equilibrium constant in terms of the partial pressures of the reactants and products, consider the general gaseous reaction,

$$\alpha A + bB + \ldots \rightleftharpoons cC + dD + \ldots$$

If P_A, P_B, P_C and P_D are the partial pressures of the various gaseous species at equilibrium, equilibrium constant may be written as,

$$K_p = \frac{P_C^{c} . P_D^{d}}{P_A^{\alpha} . P_B^{b}} \qquad \ldots (10.20)$$

where K_p is the equilibrium constant in terms of partial pressure and is constant at a given temperature. It should be noticed that equation (10.20) is valid for a system involving ideal gases.

10.5. RELATIONSHIP BETWEEN K_p AND K_c

K_p and K_c for a given reaction are not same numerically. It is possible to obtain a relationship between these two constants at any temperature provided the gases in the reaction obey the ideal gas laws. Since for an ideal gas, the pressure is given by

$$P = \left(\frac{n}{V}\right) RT$$

where V is the volume occupied by n moles of gas at the temperature T. But $\frac{n}{V}$ is equal to the molar concentration C, therefore,

$$P = CRT$$

Substituting this value of P in equation (10.20), we get

$$K_p = \frac{C_C^{c}\,(RT)^{c} \,.\, C_D^{d}\,(RT)^{d} \ldots}{C_A^{\alpha}\,(RT)^{\alpha} \,.\, C_B^{b}\,(RT)^{b} \ldots}$$

$$= \frac{C_C^{c} . C_D^{d} \ldots (RT)^{c+d \ldots}}{C_A^{\alpha} . C_B^{b} \ldots (RT)^{\alpha+b \ldots}}$$

$$= \frac{C_C^{c} . C_D^{d} \ldots}{C_A^{\alpha} . C_B^{b} \ldots}\,(RT)^{(c+d+\ldots)-(\alpha+b+\ldots)} \qquad \ldots (10.21)$$

But, since
$$K_c = \frac{C_C^{c} . C_D^{d}}{C_A^{\alpha} . C_B^{a}}$$

Therefore, equation (10.21) becomes

$$K_p = K_c (RT)^{\triangle n} \qquad \ldots (10.22)$$

where $\triangle n = [(c+d+\ldots) - (\alpha+b)\ldots]$ is equal to the difference in the total number of moles of gaseous products and reactants during the reaction. $\triangle n$ can be zero, positive or negative.

When $\triangle n$ is zero, i.e., when the number of molecules of the reactants is equal to the number of molecules of products, it follows from equation (10.22) that $K_p = K_c$.

When $\triangle n$ is positive, i.e., when the number of molecules of the products are larger than the number of molecules of the reactants, K_p is greater than K_c.

When $\triangle n$ is negative, i.e., when the number of molecules of the products are smaller than the number of molecules of the reactants, K_p is less than K_c.

Problem 10.1. For the dissociation of water, $H_2O \rightleftharpoons H_{2(g)} + \frac{1}{2}O_{2(g)}$ at 1000°C, the value of K_p with partial pressures in atmosphere is 1.87×10^{-6}. Assuming ideal behaviour of gases, calculate the corresponding value of K_c with concentrations in moles per litre.

Solution. For the reaction, $H_2O_{(g)} \rightleftharpoons H_{2(g)} + \frac{1}{2}O_{2(g)}$

$$\triangle n = 1 + \tfrac{1}{2} - 1 = \tfrac{1}{2}$$

$$T = 1500 + 273 = 1773 \text{ K}$$

and

$$R = 0.08205 \text{ litre} - \text{atm-deg}^{-1} \text{ mole}^{-1}$$

Therefore, using equation (10.22) we get

$$K_p = K_c\,(0.08205 \times 1773 \text{ K})^{1/2}$$

or

$$K_c = \frac{1.87 \times 10^{-6}}{(0.08205 \times 1773)^{1/2}}$$

$$= 1.55 \times 10^{-7} \text{ mole per litre.}$$

10.6. PROPERTIES OF EQUILIBRIUM CONSTANTS, K_p AND K_c

The equilibrium constant K_p or K_c of a reaction is generally referred to as 'classical constant' in contrast to thermodynamic constant defined by equation (10.18). The equations for K_p and K_c are applicable to the systems which involve ideal gases. Following are some of the properties of the two equilibrium constants:

(*i*) The expressions for K_p and K_c are valid only at *equilibrium*. In other words, the expression for K_p or K_c will be constant when we take only those pressure terms or concentration terms of a reversible process which correspond to the point of equilibrium. Thus, the equilibrium constant for a reaction does not depend upon the initial concentrations of reactants or products and gives constant value when equilibrium concentrations are inserted in the expression for K_c, no matter there may be different initial concentrations at the same temperature.

(*ii*) The equilibrium constant varies only with the temperature of the reaction and is constant at a constant temperature.

(*iii*) By knowing the values of K_p and K_c, we can determine the extent to which a particular reaction can take place under the given conditions. The large values of K_p and K_c imply that the formation of product is large and the reaction is more on the right side. On the other hand, if the values of K_p and K_c are small there is little product formation and the reaction is more on the left side.

(*iv*) It is possible to predict quantitatively the effect of changing concentrations of reactants and products on the extent of reaction.

Consider, for example, the reaction

$$H_{2(g)}+I_{2(g)}\rightleftharpoons 2HI_{(g)}$$

at a constant temperature. K_p for this reaction is given by

$$K_p=\frac{p^2_{HI}}{p_{H_2}.p_{I_2}}$$

Let the equilibrium be disturbed by adding H_2 at constant temperature. This will increase the pressure of hydrogen. Since K_p is constant at all pressures therefore, in order to maintain its constancy, the increase in the partial pressure of hydrogen should be compensated. This can be done by decreasing the partial pressure of iodine and increasing the partial pressure of hydrogen iodide. In order to accomplish it, hydrogen and iodine should react further to give more of hydrogen iodide and the process continuing till the equilibrium is re-established. Similar will be the effect of adding iodine. On the other hand, if hydrogen iodide is added, the numerator of the equilibrium expression increases and, therefore, the denominator must increase due to dissociation of hydrogen iodide to form H_2 and I_2 so as to maintain a constant value of K_p.

10.7. THE LE-CHATELIER-BRAUN PRINCIPLE

This principle is useful in determining the effect of variation in temperature, pressure and concentration on the position of equilibrium of a reversible reaction. This principle which is fundamentally based on the second law of thermodynamics, is defined in the following way:

If a change occurs in one of the variables, such as pressure, temperature or concentration, under which a system is in equilibrium, the system will always react in a direction which will tend to counteract the effect of change in the variable under consideration.

Consider for example, the effect of changing pressure on the system in equilibrium. An increase in the pressure of a gaseous mixture at equilibrium will cause a decrease in the volume. Therefore, the system will move in such a manner so as to favour smaller volume. In the formation of ammonia ($N_2+3H_2\rightleftharpoons 2NH_3$), there is a decrease from four volumes to two volumes. Hence, the formation of ammonia is favoured by an increase in pressure.

Similarly, we can understand the effect of temperature. For endothermic reactions, which absorb heat, an increase in temperature will be favoured. Conversely, exothermic reactions (where heat is given out) are favoured by the removal of heat.

On the other hand if a reaction, such as $N_2O_4 \rightleftharpoons 2NO_2$ is accompanied by increase in volume, the formation of product will be favoured by the decrease in pressure.

In the reaction resulting in the formation of sulphur trioxide according to the following chemical equation,

$$2\,SO_{2(g)} + O_{2(g)} \rightleftharpoons 2\,SO_{3(g)} + 42{,}000 \text{ cals}$$

Since this is an exothermic reaction, formation of sulphur trioxide will be favored by lowering the temperature.

Again if the concentration of one of the components of the system is increased, the equilibrium will change in such a way so as to decrease the concentration of that particular component.

The Le-Chatelier-Braun Principle is a principle of broad and general utility and is applicable not only to chemical equilibria but to equilibrium states in any physical system. It does not tell the quantitative change, but qualitatively it tells the change in direction of the system.

10.8. TYPES OF CHEMICAL EQUILIBRIA

There are two types:

(*i*) **Homogeneous equilibria** in which only one phase occurs. For example, a system containing only gases or a single liquid or solid phase.

(*ii*) **Heterogeneous equilibria** in which more than a single phase appears.

For example, equilibrium between solid and gas, liquid and gas, solid and liquid, solid and solid, immiscible liquids etc.

10.9. APPLICATION OF LAW OF MASS ACTION TO HOMOGENEOUS GASEOUS EQUILIBRIA

Type I. Reactions in which there is no change in the number of molecules.

In this type, the number of molecules of reactants is the same as the number of molecules of products. Some examples are

$$H_2 + I_2 \rightleftharpoons 2HI$$
$$N_2 + O_2 \rightleftharpoons 2NO$$
$$H_2 + CO_2 \rightleftharpoons H_2O + CO$$

In all such reactions, $\Delta n = 0$. Hence from equation (10.22), the equilibrium constants K_p and K_c will be equal for reversible reactions of this type.

Hydrogen iodide-equilibrium. Let us start with a moles of hydrogen and b moles of iodine and let x is the amount of hydrogen iodide formed at equilibrium. If V is the volume of the system, then the various concentration terms at equilibrium are given by

$$C_{H_2}=\frac{a-x}{V},$$

$$C_{I_2}=\frac{b-x}{V}$$

and $$C_{HI}=\frac{2x}{V}$$

The equilibrium may be represented as follows.

Initial molar concentrations	a/V		b/V		0
	H_2	$+$	I_2	$\rightleftharpoons$	$2HI$
Equilibrium molar concentrations	$\frac{a-}{V}$		$\frac{b-x}{V}$		$\frac{2x}{V}$

The equilibrium constant for this reaction is, thus, given by

$$K_c=\frac{C^2{}_{HI}}{C_{H_2}.C_{I_2}}=\frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)}=\frac{4x^2}{(a-x)\,(b-x)}\quad\ldots\ (10.23)$$

It should be noted that the volume V has disappeared from equation (10.23). This is characteristic of all reactions in which the total number of moles of reactants are equal to the total number of moles of products. Hence, *the equilibrium constant remains unchanged by change of volume and pressure*.

The equilibrium constant in terms of pressure, K_p can be determined as given below:

Initial number of moles	a		b		0
	H_2	$+$	I_2	$\rightleftharpoons$	$2HI$
Number of moles at equilibrium	$a-x$		$b-x$		$2x$

Total number of moles of gas present at equilibrium is

$$n_t=a-x+b-x+2x=a+b$$

If the total equilibrium pressure is P, then by means of Dalton's Law of Partial Pressure, the various partial pressures are given by:

$$P_{H_2}=\frac{(a-x)}{(a+b)}\,P$$

$$P_{I_2}=\frac{(b-x)}{(a+b)}\,P$$

and $$P_{HI}=\frac{(2x)}{(a+b)}\,P$$

Therefore,

$$K_p = \frac{P^2_{\mathrm{HI}}}{P_{\mathrm{H_2}} \cdot P_{\mathrm{I_2}}}$$

$$= \frac{\left(\frac{2x}{a+b}\right)^2 \cdot P^2}{\frac{(a-x)}{(a+b)} P \cdot \frac{(b-x)}{(a+b)} P}$$

$$= \frac{\frac{4x^2}{(a+b)^2} P^2}{\frac{(a-x)(b-x)}{(a+b)^2} \cdot P^2}$$

$$= \frac{4x^2}{(a-x)(b-x)} \qquad \ldots (10.24)$$

Hence, as can be seen from equations (10 23) and (10.24),

$$K_p = K_c.$$

Experimental verification of the law of mass action. This was done by Bodenstein in 1897 when he studied hydrogen iodide equilibria. He heated a known amount of hydrogen and iodine together in various proportions in sealed glass tubes to a temperature of about 450°C by keeping the bulbs in a boiling sulphur bath. After sometimes, sufficient for the attainment of equilibrium, the tubes were suddenly cooled to fix the equilibrium. The unreacted contents were then analysed by opening the bulbs in KOH solution; which absorbed unreacted iodine and hydrogen iodide formed in the reaction. The amount of hydrogen left was then determined by measuring the volume.

The value of K_c for various initial concentrations of H_2 and I_2 was then determined from equation (10.21). It was always found to be constant.

Bodenstein further confirmed the results by approaching the equilibrium from the opposite direction. He heated hydrogen iodide alone to the same temperature and determined the amounts of hydrogen and iodine formed. Let n be the initial number of moles of hydrogen iodide and α is its degree of dissociation at equilibrium. If V is the total volume, the equilibrium is represented as

Initial molar concentration	n/V	0	0
	$2\mathrm{HI} \rightleftharpoons$	$\mathrm{H_2}$ +	$\mathrm{I_2}$
Molar concentration at equilibrium	$\frac{n(1-\alpha)}{V}$	$\frac{1}{2} \cdot \frac{n\alpha}{V}$	$\frac{1}{2} \cdot \frac{n\alpha}{V}$

The equilibrium constant, K'_c, for this is given by

$$K'_c=\frac{C_{H_2}.C_{I_2}}{C^2_{HI}}$$

$$=\frac{\frac{1}{2}\frac{n\alpha}{V}\cdot\frac{1}{2}\frac{n\alpha}{V}}{\left[\frac{n(1-\alpha)}{V}\right]^2}$$

$$=\frac{\alpha^2}{4(1-\alpha)^2}$$

The equilibrium constants for direct and reverse reactions at the same temperature are related to each other by this expression.

The results of hydrogen iodide equilibrium at 457.6°C are shown in Table 10.1.

TABLE 10.1

$C_{H_2}\times10^3$ moles/litre	$C_{I_2}\times10^3$ moles/litres	$C_{HI}\times10^3$ moles/litre	K_c
5.617	0.5936	12.70	48.4*
4.580	0.9733	14.86	49.5*
3.841	1.524	16.87	48.6*
1.433	1.433	10.00	48.7**
1.696	1.696	11.81	48.5**
4.213	4.217	29.43	48.8**

*Equilibrium approached from hydrogen and iodine.

**Equilibrium approached from hydrogen iodide.

It can be seen from this table that the value of K_c are considerably constant although equilibrium was approached from different amounts of both the reactants and products.

This verifies law of mass action.

Problem 10.2. 15 gram molecules of H_2, on interaction with 5.2 gram molecules of iodine vapors at 444°C, produced 10 gram molecules of HI. Determine the equilibrium constant of the reaction

$$H_2+I_2 \rightleftharpoons 2HI$$

Solution.

$$\begin{array}{ccccc} H_2 & + & I_2 & \rightleftharpoons & 2HI \\ a & & b & & 0 \\ (a-x) & & (b-x) & & 2x \end{array}$$

In the present case,

$$a=15,\ b=5.2$$

and

$$2x=10 \quad \text{or} \quad x=5$$

Therefore,

$$a-x=15-5=10$$

$$b-x=5.2-5=0.2$$

Applying the law of Mass Action,

$$K_c = \frac{C^2_{HI}}{C_{H_2} \cdot C_{I_2}}$$

$$= \frac{(10)^2}{(10)\,(0.2)} = 50$$

Problem 10.3. The degree of dissociation of 2.40 moles of hydrogen iodide at 448°C was found to be 22 per cent. Calculate the number of moles of hydrogen iodide, hydrogen and iodine formed at equilibrium. Also calculate the equilibrium constant for the dissociation reaction.

Solution. The reaction is

$$\begin{array}{cccccc} 2HI & \rightleftharpoons & H_2 & + & I_2 \\ n(1-\alpha) & & \frac{n(\alpha)}{2} & & \frac{n(\alpha)}{2} \end{array}$$

Here $n = 2.40$ moles

and $\alpha = 0.22$

At equilibrium,

Number of moles of hydrogen iodide

$$= n(1-\alpha) = 2.40\,(1-0.2)$$
$$= 1.872$$

Number of moles of hydrogen

$$= 2.40 \times \frac{(0.22)}{2} = 0.264$$

Number of moles of iodine

$$= 2.40 \times \frac{(0.22)}{2} = 0.264$$

Again, to calculate the equilibrium constant for the reaction, let V litres be the volume of the reaction vessel.

$$K_c = \frac{\frac{n\alpha}{V} \cdot \frac{n\alpha}{V}}{\frac{[2n(1-\alpha)]^2}{V^2}} = \frac{\alpha^2}{4(1-\alpha)^2}$$

$$= \frac{(0.22)^2}{4(1-0.22)^2} = 0.0199.$$

Problem 10.4. A mixture containing 25 moles of hydrogen and 18 moles of iodine was heated in a sealed tube at 256°C till equilibrium, when 30.8 moles of hydrogen iodide was obtained. Calculate the degree of dissociation of hydrogen iodide at 456°C.

Solution. Formation of hydrogen iodide is represented as below

$$\begin{array}{ccccc} a & & b & & 0 \\ H_2 & + & I_2 & \rightleftharpoons & 2HI \\ (a-x) & & (b-x) & & 2x \end{array}$$

and in the present case, $2x = 30.8$ or $x = 15.4$, $a = 25$

$b = 18$

∴ Equilibrium constant,

$$K_c = \frac{(2x)^2}{(a-x)(b-x)}$$

$$= \frac{(30.8)^2}{(25-15.4)(18-15.4)} = 38.$$

Dissociation of hydrogen iodide is represented as below

$$2HI \rightleftharpoons H_2+I_2$$

If we start with 1 mole of hydrogen iodide and assume that α is its degree of dissociation, the equilibrium constant is given by

$$\frac{2}{4(1-\alpha)^2}=\frac{1}{K_c}=\frac{1}{38}$$

or

$$\alpha=0.245.$$

Formation of Nitric Oxide

Nitric oxide is obtained from Nitrogen and Oxygen according to the equation

$$N_2+O_2 \rightleftharpoons 2NO$$

This is a reversible process and hence the law of mass action can be applied to it.

The expressions for K_c and K_p for this reaction can be obtained exactly in the same way as were obtained in the case of hydrogen iodide equilibrium.

The Water Gas Equilibrium

This is again a reversible gaseous reaction and is represented by the equation

$$CO_2+H_2 \rightleftharpoons CO+H_2O$$

Let us start with a moles of carbon dioxide and b moles of hydrogen and let x is the amount of each of carbon monoxide and water formed at equilibrium. If V is the volume of the system then the various concentration terms at equilibrium are given by

$$C_{CO_2}=\frac{a-x}{V}; \qquad C_{H_2}=\frac{b-x}{V};$$

$$C_{CO}=\frac{x}{V}$$

and

$$C_{H_2O}=\frac{x}{V}$$

The equilibrium constant in terms of concentration for the water gas reaction is then given by

$$K_c=\frac{C_{CO}\cdot C_{H_2O}}{C_{CO_2}\cdot C_{H_2}}$$

$$=\frac{\frac{x}{V}\cdot\frac{x}{V}}{\left(\frac{a-x)}{1}\right)\left(\frac{b-x}{V}\right)}$$

$$=\frac{x^2}{(a-x)(b-x)} \qquad \ldots(10.25)$$

The equilibrium constant in terms of pressure can also be obtained as given below:

$$\begin{array}{lcccc} \text{Initial number of moles} & a & b & 0 & 0 \\ & CO_2 + & H_2 \rightleftharpoons & CO + & H_2O \\ \text{Number of moles at equilibrium} & a-x & b-x & x & x \end{array}$$

Therefore, total number of moles at equilibrium,

$$n_t = a-x+b-x+x+x = a+b$$

If the total equilibrium pressure is P, then by means of Dalton's Law of partial pressure, the various partial pressures are given by

$$P_{CO_2} = \frac{(a-x)}{(a+b)} P$$

$$P_{H_2} = \frac{(b-x)}{(a+b)} P$$

$$P_{CO} = \frac{(x)}{(a+b)} P$$

and $$P_{H_2O} = \frac{(x)}{(a+b)} P$$

Now since, $$K_p = \frac{P_{CO} . P_{H_2O}}{P_{CO_2} . P_{H_2}}$$

$$= \frac{\frac{(x)}{(a+b)} P . \frac{(x)}{(a+b)} P}{\frac{(a-x)}{(a+b)} P \ \frac{(b-x)}{(a+b)} P}$$

$$= \frac{x^2}{(a-x)(b-x)} \qquad \ldots (10.26)$$

As can be seen from equations (10.25) and (10.26) $K_p = K_c$. It should be noted that in Type I reactions, the equilibrium constant expressions do not involve any volume term and hence are independent of any pressure or volume change.

Problem 10.5. Starting with equimolar amounts of carbon monoxide and steam, calculate the molar percentage composition of the water gas system at equilibrium at 1000 K; the equilibrium constant at this temperature is 0.719.

Solution. Since the number of moles of CO and H_2O are equal at the commencement, they must obviously remain equal throughout the reaction; let these values be n_1 at equilibrium. Similarly, the number of moles of CO_2 and H_2 must be equal; let these be n_2 at equilibrium. It follows, then, from expression for the equilibrium constant,

$$K = \frac{n_{CO} \cdot n_{H_2O}}{n_{CO_2} . n_{H_2}}$$

Substituting the various values, we get

$$0.719 = \frac{n_1^2}{n_2^2} \qquad \text{or} \qquad \frac{n_1}{n_2} = \sqrt{0.719} = 0.848$$

The amonuts of CO, H_2O, CO_2 and H_2 at equilibrium are, therefore, present in the molar ratio of 0.848: 0.848: 1.00 : 1.00; the molar precentage of CO and H_2O are consequently each

$$\frac{0.848}{(2\times0.848)+(2\times1.00)}\times100=22.9\%$$

The molar percentages of CO_2 and H_2 are then each 27.1 per cent. The composition of the water gas at equilibrium at 1000 K is thus CO, 22.9; H_2O, 22.9; CO_2, 27.1 and H_2; 27.1 moles per cent.

Type II. Reactions in which there is a change in the number of molecules. In this type, the number of molecules of reactants is not equal to the number of molecules of products. Some examples of this type are

$$PCl_5 \rightleftharpoons PCl_3+Cl_2$$
$$N_2+3H_2 \rightleftharpoons 2NH_3$$
$$N_2O_4 \rightleftharpoons 2NO_2$$
$$COCl_2 \rightleftharpoons CO+Cl_2 \text{ (dissociation of phosgene)}$$
$$2SO_2+O_2 \rightleftharpoons 2SO_3$$
$$2H_2S \rightleftharpoons 2H_2+2S$$

In all these reactions, there is a change in the number of molecules. Hence $K_p \neq K_c$.

We shall study some of the reactions in detail.

Dissociation of Phosphorus Pentachloride

Let us start with n moles of PCl_5 and let α is the degree of dissociation of PCl_5. If V is the volume of the system, then the equilibrium is represented by

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
Initial molar concentration	$\frac{n}{V}$		0		0
Equilibrium molar concentration	$\frac{n(1-\alpha)}{V}$		$\frac{n\alpha}{V}$		$\frac{n\alpha}{V}$

The equilibrium constant in terms of concentration is given by

$$K_c=\frac{C_{PCl_3}\,.\,C_{Cl_2}}{C_{PCl_5}}$$

$$=\frac{\frac{n\alpha}{V}\,.\,\frac{n\alpha}{V}}{\frac{n(1-\alpha)}{V}}=\frac{n\alpha^2}{(1-\alpha)V} \qquad \ldots (10.27)$$

It should be noted that V occurs in the denominator. Hence as V increases, $\frac{\alpha^2}{(1-\alpha)}$ must also increase to maintain constancy of K_c. This means that an increase in volume (or decrease in pressure) will increase the degree of dissociation. This is also confirmed when equilibrium constant in terms of pressure is calculated. This is shown below:

	PCl_5	$\rightleftharpoons$	PCl_3	Cl_2
Initial number of moles	n		0	0
Number of moles at equilibrium	$n(1-\alpha)$		$n\alpha$	$n\alpha$

Total number of moles at equilibrium,

$$n_t = n - n\alpha + n\alpha + n\alpha$$

$$= n(1+\alpha)$$

Let the equilibrium pressure is P.

Therefore, the various partial pressures are given by

$$P_{PCl_5} = \left[\frac{n(1-\alpha)}{n(1+\alpha)}\right]P = \left(\frac{1-\alpha}{1+\alpha}\right)P$$

$$P_{PCl_3} = \left[\frac{n\alpha}{n(1+\alpha)}\right]P = \left(\frac{\alpha}{1+\alpha}\right)P$$

and

$$P_{Cl_2} = \left[\frac{n\alpha}{n(1+\alpha)}\right]P = \left(\frac{\alpha}{1+\alpha}\right)P$$

Hence

$$K_p = \frac{P_{PCl_3} \,.\, P_{Cl_2}}{P_{PCl_5}}$$

$$= \frac{\left(\frac{\alpha}{1+\alpha}\right)P \cdot \left(\frac{\alpha}{1+\alpha}\right)P}{\left(\frac{1-\alpha}{1+\alpha}\right)P}$$

or

$$K_p = \frac{\alpha^2}{1-\alpha^2} \cdot P \qquad \ldots (10.28)$$

From this equation, it can easily be shown that a decrease in P will increase α. This is also in agreement with Le-Chatelier Braun Principle.

Dissociation of Nitrogen Tetraoxide

Let n is the initial number of moles of nitrogen tetraoxide and let α be the degree of dissociation at equilibrium. The total volume of the system is V. The equilibrium is represented as,

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial number of moles	n		0
Number of moles at equilibrium	$n(1-\alpha)$		$2n\alpha$

$$\therefore \qquad K_c = \frac{C^2_{NO_2}}{C_{N_2O_4}} = \frac{\left(\frac{2n\alpha}{V}\right)^2}{\frac{n(1-\alpha)}{V}}$$

$$= \frac{4n\alpha^2}{(1-\alpha)V}$$

Again, $$K_p = \frac{P^2_{NO_2}}{P_{N_2O_4}}$$

Total number of moles at equilibrium

$$= n(1-\alpha) + 2n\alpha = n(1+\alpha)$$

If the total equilibrium pressure is P, the partial pressures of the various gases are given by

$$P_{NO_2} = \left[\frac{2n\alpha}{n(1+\alpha)}\right]P = \left(\frac{2\alpha}{1+\alpha}\right)P$$

and $$P_{N_2O_4} = \left[\frac{n(1-\alpha)}{n(1+\alpha)}\right]P = \left(\frac{1-\alpha}{1+\alpha}\right)P$$

$$\therefore \quad K_p = \frac{\left[\left(\frac{2\alpha}{1+\alpha}\right)P\right]^2}{\left(\frac{1-\alpha}{1+\alpha}\right)P} = \frac{4\alpha^2 P}{1-\alpha^2} \qquad \ldots (10.29)$$

The effect of pressure change is similar as in the case of dissociation of PCl_5. From equation (10.29), it is evident that from a knowledge of K_p, degree of dissociation at any pressure can be calculated.

The Ammonia Equilibria. Ammonia is obtained by combining one part of nitrogen with three parts of hydrogen. The reaction is reversible as shown below:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Let us start with 1 mole of nitrogen and 3 moles of hydrogen in a closed vessel of volume V and let x moles be the amount of ammonia at equilibrium.

The various concentration terms at equilibrium are given by

$$C_{N_2} = \frac{1-x}{V}; \; C_{H_2} = \frac{3-3x}{V}$$

and $$C_{NH_3} = \frac{2x}{V}$$

Therefore, equilibrium constant in terms of concentration is given by

$$K_c = \frac{C^2_{NH_3}}{C_{N_2}.\, C^3_{H_2}}$$

$$= \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)\left(\frac{3-3x}{V}\right)^3}$$

$$= \frac{4x^2V^2}{27(1-x)^4} \qquad \ldots (10.30)$$

To calculate the equilibrium constant in terms of pressure, *i.e.*, K_p we proceed as follows:

At equilibrium:

Number of moles of N_2 $= 1 - x$
Number of moles of H_2 $= 3 - 3x = 3(1-x)$
Number of moles of NH_3 $= 2x$
Therefore, the total number of moles

$$= 1 - x + 3 - 3x + 2x = 4 - 2x$$

If P is the total equilibrium pressure, the partial pressures of the various gases are given by

$$P_{N_2} = \frac{(1-x)}{(4-2x)} P$$

$$P_{H_2} = \frac{3(1-x)}{4-2x} P$$

and

$$P_{NH_3} = \frac{2x}{4-2x} P$$

$$K_p = \frac{P_{NH_3}}{P_{N_2} \cdot P^3_{H_2}}$$

$$= \frac{\left(\frac{2x}{4-2x}\right)^2 P^2}{\frac{(1-x)}{(4-2x)} P \cdot \left[\frac{3(1-x)}{4-2x}\right]^3 P^3}$$

$$= \frac{4x^2 (4-2x)^2}{27(1-x)^4 P^2} \qquad \ldots (10.31)$$

If x is negligibly small as compared to unity, then equation (10.31) becomes

$$K_p = \frac{64x^2}{27P^2} \quad \text{or} \quad x^2 = \frac{27}{64} K_p P^2$$

From this, it is clear that $x \propto P$ (K_p is constant at constant temperature)

In other words, the formation of ammonia increases with increase of pressure. This is also evident from Le-Chatelier Braun Principle according to which the formation of ammonia is favoured by an increase of pressure (since formation of ammonia is attended by a decrease in volume from 4 molar volumes to two molar volumes). Hence in the synthesis of ammonia, a pressure of 200 atmospheres or more, is used in practice.

Problem 10.6. In a mixture of 1 part of N_2 to 3 parts of H_2, the mole per cent of NH_3 at equilibrium was found to be 1.20 at 500°C at a total pressure of 10 atm. Calculate the value of K_p and the pressure at which the equilibrium mixture at this temperature contains 10.4 mole per cent of NH_3.

Solution. Let x be the mole fraction of NH_3 at equilibrium, so that $100x$ is the mole per cent. The sum of the mole fractions of N_2 and H_2 must then be $1-x$, and since these gases are in the ratio of 1 to 3, it follows that

$$X_{N_2}=\frac{1}{4}(1-x) \text{ and } \qquad X_{H_2}=\frac{3}{4}(1-x)$$

and so, if P is the total pressure,

$$K_p=\frac{P^2_{NH_3}}{P_{N_2}\times P^3_{H_2}}$$

$$=\frac{(xP)^2}{\frac{1}{4}(1-x)P\times\left(\frac{3}{4}(1-x)P\right)^3}$$

In the present example, P is 10 atm;

$100x$ is 1.20 so that $\quad x=0.0120$

and $\quad 1-x=0.988.$

Consequently, $$K_p=\frac{(0.0120\times 10)^2}{\left(\frac{1}{4}\times 0.988\times 10\right)\left(\frac{3}{4}\times 0.988\times 10\right)^3}$$

$$=1.43\times 10^{-5}$$

with the pressure in atm.

It is now required to calculate P corresponding to $100x=10.4$

i.e., $\quad x=0.104$ and $1-x=0.896$; thus

$$K_p=1.43\times 10^{-5}$$

$$=\frac{(0.104\times P)^2}{\left(\frac{1}{4}\times 0.896\times P\right)\times\left(\frac{3}{4}\times 0.896\times P\right)^3}$$

or $\quad P=105$ atm.

10.10. DEGREE OF DISSOCIATION FROM DENSITY MEASUREMENTS

Consider the reaction

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Let D be the density of PCl_5 before dissociation and d be the density after dissociation.

Suppose we start with 1 mole of PCl_5 and let α is the degree of dissociation of PCl_5. The total number of moles at equilibrium will be $1-\alpha+\alpha+\alpha=1+\alpha$. If V is the volume occupied by 1 mole of PCl_5 under the temperature and pressure of the experiment, the volume occupied by $1+\alpha$ moles at equilibrium would be $(1+\alpha)\ V$. Since density is inversely proportional to volume, we have

$$D \propto \frac{1}{V} \qquad \ldots (10.32)$$

and $$d \propto \frac{1}{(1+\alpha)\ V} \qquad \ldots (10.33)$$

Dividing (10.32) by (10.33), we have

$$\frac{D}{d}=\frac{(1+\alpha)V}{V};\quad \alpha=\frac{D}{d}-1$$

or

$$\alpha=\frac{D-d}{d} \qquad \text{..(10.34)}$$

If a molecule dissociates into n number of moles, the total number of moles at equilibrium after dissociation will be $(1-\alpha+n\alpha)$ and equation (10.34) takes the form

$$\alpha=\frac{1}{(n-1)}\left(\frac{D-d}{d}\right) \qquad \text{...(10.35)}$$

Problem 10 7. Phosphorus pentachloride when heated in a closed vessel dissociates into PCl_3 and Cl_2. The gaseous mixture is found to have density of 75.5 at 200°C. Find the degree of dissociation of PCl_5 at the same temperature. [Atomic Weight, P=31; Cl=35.5].

Solution. We have the relation

$$\alpha=\frac{D-d}{d}$$

Here, density (D) of PCl_5 before dissociation is given by

$$\frac{\text{Molecular Weight}}{2}=\frac{31+177.5}{2}=104.25$$

and

$$d=75.5.$$

$$\alpha=\frac{104.25-75.5}{75.5}=0.381 \quad \text{or} \quad 38.1\%$$

10.11. COMBINATION OF EQUILIBRIA

It is sometimes possible to calculate the equilibrium constant for a reaction from a knowledge of the equilibrium constant of other reactions having some reactants or products common. Consider, for example, the dissociation of water and the water-gas equilibrium which takes place as given below:

$$H_2O \rightleftharpoons H_2+\tfrac{1}{2}O_2,\ K_p=\frac{P_{H_2}\cdot P_{O_2}^{\frac{1}{2}}}{P_{H_2O}} \qquad \text{...(10.36)}$$

$$CO_2+H_2 \rightleftharpoons H_2O+CO,\ K_p'=\frac{P_{H_2O}\quad P_{CO}}{P_{CO_2}.\ P_{H_2}} \qquad \text{...(10.37)}$$

Knowing K_p and K_p' for these two reactions, it is possible to calculate the equilibrium constant, K_p'' for the reaction.

$$CO_2 \rightleftharpoons CO+\tfrac{1}{2}O_2,\ K_p''=\frac{P_{CO}\ .\ P_{O_2}^{\frac{1}{2}}}{P_{CO_2}} \qquad \text{...(10.38)}$$

It is apparent from equations (10.36), (10.37) and (10.38) that

$$K_p''=K_p'\ .\ K_p \qquad \text{...(10.39)}$$

By using equations similar to type (10.39), it is possible to determine the equilibrium constant for a reaction which cannot be obtained by direct measurement with accuracy. The only condition is that the temperature at which various equilibrium constants are measured must remain constant.

10.12. THE EFFECT OF INERT GAS (A GAS WHICH DOES NOT ENTER INTO THE REACTION) ON EQUILIBRIUM

This will depend upon the type of reaction. In reactions of type I ($\triangle n=0$), addition of an inert gas will simply increase the total pressure of the system without changing the partial pressures of various reacting species. But, as we have seen earlier, reactions of type I remain unaffected by change of pressure. Hence the addition of inert gas to such type of reactions will not effect the extent of reaction at equilibrium.

In reactions of type II ($\triangle n \neq 0$), the addition of an inert gas does effect the extent of reaction at equilibrium because it decreases the partial pressures of the reactants and products of a given total equilibrium pressure. Consider, for example, the dissociation of phosporus pentachloride:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

The equilibrium constant expressions in terms of pressure and concentration for this reaction are

$$K_p = \frac{\alpha^2 P}{1-\alpha^2} \; ; \; K_c = \frac{n\alpha^2}{(1-\alpha)} V$$

Let us now consider two cases:

(*i*) If an inert gas is added at constant volume, the various equilibrium concentration terms involved are not changed. Since, the concentration of an inert gas is not involved in the equilibrium constant expression, therefore, the equilibrium remains unchanged.

(*ii*) If an inert gas is added at constant pressure, the volume V of the system will increase. This will cause dilution of the reactants and products. From the expression for K_c, if V varies, α must increase to keep K_c constant. This means that more of phosphorus pentachloride will dissociate, or in the other words, the formation of the product is favoured.

In general we can say that for those reactions in which the number of molecules of products are more than those of reactants, addition of an inert gas at constant pressure will favour the product formation. However, for reactions in which $\triangle n$ is negative, for example, in the formation of ammonia, addition of an inert gas at constant pressure will favour the formation of reactants.

10.13 HOMOGENEOUS EQUILIBRIA IN LIQUID SYSTEMS

An important example of this type of equilibrium is the esterification of acetic acid by ethyl alcohol. The reaction takes place as follows:

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Let a moles of acetic acid and *b* moles of ethyl alcohol are heated together in a sealed tube at 100°C so that the equilibrium is reached. Let *x* moles of ethyl acetate is formed at equilibrium. If *V* is the volume of the system then the various concentration terms at equilibrium are given by

$$C_{CH_3COOH} = \frac{a-x}{V}, \qquad C_{C_2H_5OH} = \frac{b-x}{V}$$

$$C_{CH_3COOC_2H_5} = \frac{x}{V} \text{ and } C_{H_2O} = \frac{x}{V}$$

The equilibrium constant is given by

$$K_c = \frac{C_{CH_3COOC_2H_5} \cdot C_{H_2O}}{C_{CH_3COOH} \cdot C_{C_2H_5OH}}$$

$$= \frac{\frac{x}{V} \cdot \frac{x}{V}}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)}$$

$$= \frac{x^2}{(a-x)(b-x)}$$

We see that the expression for K_c does not contain any volume terms. Hence K_c is not affected by the change of volume.

In the deduction of K_c, it is assumed that the various components are all present in dilute solution. If the solutions are concentrated, it is not advisable to use molar concentration. For concentrated solutions, better results are obtained by using (*i*) mole fractions and (*ii*) activities.

Problem 10.8. Calculate the per cent of acid that is esterified when a mixture consisting initially of 1 mole of acetic acid, 1 mole of ethanol and 1 mole of water attains equilibrium at 100°C. (K_c at 100°C is 4.0).

Solution. The equilibrium is represented as

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Let *y* be the number of moles of ester formed; the system at equilibrium then contains $1-y$ mole of acid, $1-y$ mole of alcohol, *y* mole of ester and $1+y$ mole of water. Since the equilibrium constant at 100°C is 4.0.

$$K_c = 4.0 = \frac{y(y+1)}{(1-y)(1-y)}$$

or

$$y = 0.54$$

The other value of y is impossible. Consequently 54 per cent of the acid is esterified.

Dissociation of nitrogen tetraoxide into nitrogen dioxide in chloroform solution. This is another example of homogeneous equilibria in liquid phase. The equilibria at 82°C is represented as follows:

$$\begin{array}{lcc} \text{Initial molar concentration} & \frac{a}{V} & 0 \\ & N_2O_4 & \rightleftharpoons \; 2NO_2 \\ \text{Molar concentration at equilibrium} & \frac{a-x}{V} & \frac{2x}{V} \end{array}$$

The equilibrium constant follows as:

$$K_c = \frac{C^2_{NO_2}}{C_{N_2O_4}} = \frac{\left(\frac{2x}{V}\right)^2}{\frac{a-x}{V}}$$

or

$$K_c = \frac{4x^2}{(a-x)V}$$

In this case, the expression for K_c contains volume terms. Hence, K_c is affected by change of volume.

Problem 10.9. A solution is made up of 0.50 mole of N_2O_4 in 450 ml of chloroform; calculate the concentration of NO_2 in the solution at equilibrium at 8.2°C.

Solution. Let y be the number of moles that have dissociated, leaving $0.5-y$ mole N_2O_4 and forming $2y$ mole NO_2 in 450 ml, *i.e.*, 0.45 litre. The mean value of K_c is 1.08×10^{-5}, with concentrations in moles per litre; hence,

$$K_c = 1.08 \times 10^{-5} = \frac{C^2_{NO_2}}{C_{N_2O_4}}$$

$$= \frac{\left(\frac{2y}{0.45}\right)^2}{\frac{0,5-y}{0.45}} = \frac{4y^2}{0.45(0.5-y)}$$

or

$$y = 7.8 \times 10^{-4} \text{ mole}$$

The concentration of NO_2 is $2y/0.45$

i.e.

$$\frac{2 \times 7.8 \times 10^{-4}}{0.45} = 3.5 \times 10^{-3} \text{ mole per litre.}$$

10.14. EQUILIBRIA IN HETEROGENEOUS SYSTEMS

Heterogeneous reactions involve two or more phases, one of which is a solid or liquid. The application of law of mass action to heterogeneous equilibria is based on the fact that the activity of a pure solid or liquid is always taken as unity at all temperatures up to fairly high pressures.

Consider the dissociation of calcium carbonate which is an example of solid gas equilibria. When calcium carbonate is heated in closed vessel for some time, the following equilibrium is established:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The thermodynamic equilibrium constant, K_a, for this reaction is

$$K_a = \frac{a_{CaO} \cdot a_{CO_2}}{C_{CaCO_3}} \quad \ldots (10.40)$$

where the a's represent the activities. But so long as the pressure are not too high, the activities of two solids $CaCO_3$ and CaO are unity *i.e.*, $a_{CaCO_3} = a_{CaO} = 1$, so that equation (10.40) becomes

$$K_p = a_{CO_2} \quad \ldots (10.41)$$

Again, if it is assumed that gas involved behaves ideally, the activity is proportional to its partial pressure in the equilibrium state *i.e.*, p_{CO_2} and equation (10.41) becomes

$$K_p = p_{CO_2} \quad \ldots (10.42)$$

It follows, therefore, that when dealing with heterogeneous equilibria, only the activities or pressures of the gaseous constituents are involved in writing the expression for the equilibrium constant and the presence of pure solid or liquid phases, irrespective of their amount, can be completely ignored. K_p's of heterogeneous reactions are generally called as *condensed equilibrium constants*.

Other Examples of Heterogeneous Equilibria

The dissociation of solid ammonium hydrosulphide NH_4HS. Ammonium hydrosulphide dissociates on heating into ammonia and hydrogen sulphide as shown below:

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

Applying the law of mass action and remembering that the activity of solid is unity, we get the expression for the condensed equilibrium constant K_p which is

$$K_p = p_{NH_3} \cdot p_{H_2S} \quad \ldots (10.43)$$

where p_{NH_3} and p_{H_2S} are the partial pressures of ammonia and hydrogen sulphide respectively. This equation can be tested by adding one or other of the gases to the systems in equilibrium at constant volume and determining K_p. This was always found to be constant.

The carbon disulphide equilibrium. This equilibrium which involves one solid and two gases is approached when gaseous sulphur is passed over solid carbon at high temperatures. The reaction takes place as follows:

$$C(s) + S_2(g) \rightleftharpoons CS_2(g)$$

The condensed equilibrium constant for this reaction is given by

$$K_p = \frac{p_{CS_2}}{p_{S_2}} \quad \ldots (10.44)$$

Dissociation of mercuric oxide. This takes place as follows:

$$HgO(s) \rightleftharpoons Hg\,(l) + \tfrac{1}{2}O_2(g)$$

We see that this equilibrium involves one solid, one liquid, and one gaseous phase. The condensed equilibrium constant for this equilibrium is given by

$$K_p = p_{O_2}^{\frac{1}{2}} \quad \ldots (10.45)$$

10.15. VARIATION OF EQUILIBRIUM CONSTANT WITH TEMPERATURE

Equilibrium constant of a reaction, although constant at a given temperature, varies appreciably with temperature. The effect of variation in temperature on equilibrium constant is qualitatively given by Le-Chatelier-Braun Principle. However, the exact relationship by which equilibrium constant for any type of reaction varies with temperature is readily deduced thermodynamically as follows:

In the thermodynamic derivation of equilibrium constant, it was shown that

$$\triangle G^\circ = -RT \ln K_a$$

or

$$\ln K_a = \frac{-\triangle G^\circ}{RT} \quad \ldots (10.46)$$

Differentiating this equation with respect to temperature at constant pressure, we get

$$\frac{d \ln K_a}{dT} = -\frac{1}{R}\left[\frac{d(\triangle G^\circ/T)}{dT}\right]_P \quad \ldots (10.47)$$

But since,

$$\frac{d(\triangle G^\circ/T)}{dT} = -\frac{\triangle H^\circ}{T^2} \quad \ldots (10.48)$$

Therefore, equation (10.47) becomes

$$\frac{d \ln K_a}{dT} = \frac{\triangle H^\circ}{RT^2} \quad \ldots (10.49)$$

For gaseous reactions, in which the various gases involved behave ideally, the activity terms can be replaced by the corresponding partial pressures. K_a is then replaced by K_p and equation (10.49) is written as

$$\frac{d \ln K_p}{dT} = \frac{\triangle H^\circ}{RT^2} \quad \ldots (10.50)$$

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Differentiating this equation with respect to temperature at constant pressure, we get

$$\frac{d\, ln\, K_a}{dT} = -\frac{1}{R}\left[\frac{d(\triangle G^\circ/T)}{dT}\right]_P \qquad \ldots (10.47)$$

But since,

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Therefore, equation (10.47) becomes

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For gaseous reactions, in which the various gases involved behave ideally, the activity terms can be replaced by the corresponding partial pressures. K_a is then replaced by K_p and equation (10.49) is written as

$$\frac{d\, ln\, K_p}{dT} = \frac{\triangle H^\circ}{RT^2} \qquad \ldots (10.50)$$

Equation (10.50) is known as the Van't Hoff equation and defines the temperature coefficient of $ln\ K_p$ in terms of heat of reactions ΔH° and the temperature T. Assuming ΔH° to be constant over a small range of temperature, integration of equation (10.50) yeilds,

$$ln\ K_p = -\frac{\Delta H^\circ}{RT} + \text{constant}$$

or

$$\log_{10} K_p = -\frac{\Delta H^\circ}{2.303RT} + \text{constant} \qquad \ldots (10.51)$$

The value of the constant can be determined for any reaction by substituting a known value of K_p at some given temperature. Equation (10.51) shows that a plot of $\log_{10} K_p$ *vs* $\frac{1}{T}$ should be straight line with a slope equal to $\frac{-\Delta H^\circ}{2.303\ R}$. When applied to various reversible reactions, it was found that plot was always a straight line. This indicates that ΔH° is constant for the reaction over the experimental temperature range. Consequently, it is possible to determine ΔH° by measuring the equilibrium constants over a temperature range as follows:

$$\Delta H^\circ = -2.303\ R \times \text{slope}$$

Equation (10.51) can also be integrated between the limits K_{p_2} at temperature T_2 to K_{p_1} at T_1 as follows:

$$\int_{K_{p1}}^{K_{p2}} d\ ln\ K_p = \int_{T_1}^{T_2} \frac{\Delta H^\circ}{RT}\ dT \qquad \ldots (10.52)$$

The result is

$$ln\ \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H^\circ}{R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

or

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H^\circ}{2.303\ R}\left[\frac{T_2 - T_1}{T_2 T_1}\right] \qquad \ldots (10.53)$$

From equation (10.53), it is possible to calculate K_{p_2} at T_2 if K_{p_1} at T_1 and ΔH° are given. Alternatively, if the equilibrium constants at two different temperatures are known, the heat of reaction can be determined.

While deducing equation (10.51), or equation (10.53), it was assumed that ΔH° is constant. However, for exact calculations, ΔH° should be expressed as a power series in T.

$$\Delta H^\circ = \Delta H^\circ + A'T + B'T^2 + C'T^3 \qquad \ldots (10.54)$$

where A', B', C' etc. are determined by the heat capacities of the substances involved in the reaction.

Substituting this value of $\triangle H^\circ$ in equation (10.54) we get

$$\frac{d\ ln\ K_p}{dT}=\frac{\triangle H^\circ}{RT^2}+\frac{A'}{RT}+\frac{B'}{R}+\frac{C'}{R}T+\ldots \qquad \ldots (10.55)$$

Integrating this expression, we get

$$ln\ K_p=-\frac{\triangle H^\circ}{RT}+\frac{A'}{R}\ ln\ T+\frac{B'T}{R}+\frac{C'T^2}{2R}+\ldots \qquad \ldots (10.56)$$

Equation (10.56) gives a complete expression for the variation of the equilibrium constant with temperature.

Variation of K_c with temperature. Variation of K_c with temperature is given by an equation anologous to equation (10.50) and is shown as

$$\frac{d\ ln\ K_c}{dT}=\frac{\triangle E^\circ}{RT^2} \qquad \ldots (10.57)$$

where $\triangle E^\circ$ is the heat of reaction at constant volume.

This equation can be treated in the same manner as was equation (10.57). Equations (10.50) and (10.57) will be identical only when $\triangle n=0$ (under this condition, $\triangle H^\circ=\triangle E^\circ$ and $K_p=K_c$).

Problem 10.10. The equilibrium constant K_p for the reaction

$$N_2+3H_2=2NH_3$$

is 1.64×10^{-4} at 400° C and 0.144×10^{-4} at 500°C. Calculate the mean heat of formation of 1 mole of ammonia from its elements in this temperature range.

Solution. Let T_1 be 400°C *i.e.*, 673K and
T_2 be 530°C *i.e.*, 773K; then
$(K_p)_1$ is 1.64×10^{-4}
and $(K_p)_2$ is 0.144×10^{-4}.

These values may be inserted into equation

$$\log\frac{K_{p_2}}{K_{p_1}}=\frac{-\triangle H^\circ}{2.303\ R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$
$$=\frac{\triangle H^\circ}{4.576}\left(\frac{T_2-T_1}{T_2T_1}\right)$$

To evaluate $\triangle H^\circ$ in calories for the reaction, we have

$$\log 0.144\times10^{-4}-\log 1.64\times10^{-4}=\frac{\triangle H^\circ(773-673)}{4.576\ (673\times773)}$$

or $\triangle H^\circ=25140$ cal.

This is the heat of the reaction as written, in which two moles of NH_3 are formed; the mean heat of formation of one mole of NH_3 is thus -12570 cal or -12.57 kcal.

10.16. VARIATION OF EQUILIBRIUM CONSTANT WITH PRESSURE

Both K_p and K_c do not vary with change of pressure for ideal gases.

(*i*) K_p **is independent of pressure.**

Since $$ln\ K_p=-\frac{\triangle G^\circ}{RT}$$

Differentiating this expression with respect to total pressure P, at constant temperature, we get

$$\left(\frac{d\ ln\ K_p}{dP}\right)_T=-\frac{1}{RT}\left[\frac{d(\triangle G^\circ)}{dP}\right]_T=0 \quad \ldots (10.58)$$

Since standard free energy change, $\triangle G^\circ$, of the reaction is independent of pressure and is the function of temperature only, K_p will be independent of pressure.

(*ii*) K_c **is independent of pressure.**

We have the relationship

$$K_p=K_c(RT)^{\triangle n}$$

$$ln\ K_p=ln\ K_c+\triangle n\ ln\ RT$$

or $$ln\ K_c=ln\ K_p-\triangle n\ ln\ RT \quad \ldots (10.59)$$

Differentiating with respect to total pressure P, at constant temperature, we find

$$\left(\frac{d\ ln\ K_c}{dP}\right)_T=\left(\frac{d\ ln\ K_p}{dP}\right)_T-\Delta n\left(\frac{d\ ln\ RT}{dP}\right)_T=0 \quad \ldots (10.60)$$

Since both the terms on the right hand side of this equation are independent of pressure at constant temperature, K_c is also independent of pressure.

PROBLEMS

1. What do you understand by a reversible chemical reaction? Give examples and point out conditions affecting the course of the action.

2. Periodic analysis of a mixture at equilibria shows that the concentrations of reactants and products remain unchanged. Does this indicate that the chemical reaction has ceased? Explain.

3. Give the thermodynamic derivation of the equilibrium constant; state the different units in which they are expressed.

4. (*a*) Explain with the help of two examples the 'Le-Chatelier-Braun Principle'.

(*b*) Discuss the effect of temperature and pressure on the following reactions:

(*i*) $N_2+O_2\rightleftharpoons 2NO-43{,}200$ cals.

(*ii*) $2SO_2+O_2\rightleftharpoons 2SO_3-42{,}000$ cals.

5. Equilibrium constant of the reaction $H_2+I_2\rightleftharpoons 2HI$ is 64 at a certain temperature. If 12 gm of hydrogen and 762 gm of iodine be kept in a sealed vessel at this temperature till the equilibrium is reached, what weight of HI will be present in the vessel? What effect will be observed on the weight of HI if the volume of the vessel were reduced to half?

Ans. Weight of HI found=750 gm.

6. For the reaction:

$$d+f\rightleftharpoons g+h$$

Write the expressions for K_c and K_p. What are the units for K_c (concentration given in moles) and for K_p (pressure in atmosphere).

If in the above reaction $P_d = 0.40$ atm.; $P_f = 0.30$ atm, $P_g = 0.20$ atm, $P_h = 0.10$ atm, calculate K_p.

Ans. 0.17

7. For the reaction:

$$C + D \rightleftharpoons 2E + \text{Heat}$$

(*a*) Write the expression for the equilibrium constant.

(*b*) If the equilibrium mixture is heated, which product (s) is (are) favoured?

(*c*) What is the effect of increasing in pressure on the equilibrium mixture?

(*d*) If 2.0 moles of *C* and *D* each are kept in a one litre flask and allowed to attain equilibrium, what would be the concentration of *E*, if $K = 100$?

Ans. (*d*) 3.4 moles

8. For the reaction:

$$N_2O_4 \rightleftharpoons 2NO_2 - 1{,}400 \text{ cals.}$$

calculate the percentage dissociation. The vapor density of the gas at 60°C is 30.5. Discuss the effect of increase of temperature and pressure on the above reaction.

Ans. 50.32 per cent

9. (*a*) For the reaction:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

the equilibrium constant is 46 at 490°C. If one mole of H_2 and I_2 were introduced into a litre vessel and equilibrated at 490°C, what would be the concentration of HI at equilibrium?

Ans. [HI] = 1.54

(*b*) For the reaction:

$$2a \rightleftharpoons c + d$$

the equilibrium constant is 1.9×10^{-3}. At equilibrium, the concentrations observed were:

$[c] = 1.2 \times 10^{-3}\ M$

$[d] = 3.8 \times 10^{-6}\ M$

What was $[a]$ at equilibrium?

Ans. $2.1 \times 10^{-3}\ M$

10. Calculate K_p for the reaction:

$$S_{(s)} + 2CO_{(g)} \rightleftharpoons SO_{2(g)} + 2C_{(s)}$$

At the temperature in question, 2 atm of CO are introduced into a vessel containing excess solid sulphur and a final equilibrium pressure of 1.03 atm is observed.

Ans. 270 atm^{-1}

11. Write notes on the following:

(*a*) Law of mass action.

(*b*) The effect of inert gas on equilibrium.

(*c*) Variation of equilibrium constant with temperature.

(*d*) Properties of equilibrium constants K_c and K_p.

12. Ferrous sulphate undergoes a thermal decomposition as follows:

$$2FeSO_{4(s)} \rightleftharpoons Fe_2O_{3(s)} + SO_{2(g)} + SO_{3(g)}$$

At 929K, the total gas pressure is 0.9 atm with both solids present.

(*a*) Calculate K_p for this temperature.

(*b*) Calculate the equilibrium—total pressure that will be obtained if excess ferrous sulphate is placed in a flask at 929K, which contains an initial SO_2 pressure of 0.6 atm.

Ans. 0.203 atm; 1.09 atm.

Chapter 11

PHASE EQUILIBRIA

11.1. PHASE RULE

The phase rule is a generalization which seems to explain the equilibrium existing between the heterogeneous system and was theoretically deduced by Willard Gibbs in 1876. Mathematically, it may be stated as

$$F+P=C+2$$

where F is the number of degrees of freedom, P is the number of phases and C is the number of components. This rule does not involve any assumptions as to the nature of matter and is valid provided the equilibrium between any number of phases is affected only by temperature, pressure and concentration and not by any other force such as gravitational, electrical or magnetic.

This rule, if properly applied, has no exceptions.

11.2. DEFINITIONS OF VARIOUS TERMS INVOLVED IN THE PHASE RULE

Phase. *A phase is defined as any homogeneous and physically distinct part of a system which is separated from other parts of the system by definite boundary surfaces.*

Consider, for example, the system in which ice, liquid water and water vapor are existing together. Here, each form constitutes a separate phase and is separated from other forms by definite bounding surfaces. However, each crystalline form of ice constitutes a separate phase since it is clearly marked off from the other forms. In general, every solid in a system is invariably regarded as an individual phase except in a solid solution (homogeneous) which will constitute a single phase no matter how many chemical compounds it may contain. Thus, Mohr's Salt, $FeSO_4(NH_4)_2SO_4.6H_2O$ constitutes a single phase although it consists of $FeSO_4$, $(NH_4)_2SO_4$ and H_2O. The same applies to a liquid solution. If two or any number of liquids are completely miscible with each other and form one liquid layer, it will constitute only one phase. If the two liquids are immiscible and there are two layers, as with benzene and water, there are two phases separated by a definite boundary. Similarly, if there are three immiscible liquids, there will be three phases. A gaseous system always constitutes a single phase, no matter it may consist of any number of gases because gases are always miscible and form homogeneous mixture.

Component. *The number of components of a system at equilibrium is the smallest number of independently variable constituents by means of which the composition of each phase can be expressed either directly or in the form of a chemical equation.*

Consider the water system which can have three phases: ice, liquid water and water vapor in equilibrium. The composition of each of the three phases can be expressed in terms of the component H_2O. Hence, this is a one component system. It is true that molecular complexity of water is different in the three phases but the number of components is not affected. Similarly, sulphur system is also one component system although sulphur occurs in various different forms viz., rhombic sulphur, monoclinic sulphur, liquid and vapor sulphur (each form can be expressed in terms of only one component *i.e.*, Sulphur). The same applies to acetic acid which consists entirely of double molecules in the solid state, to a great extent in the liquid and partially in the vapor; the composition of each phase can however be expressed in terms of CH_3COOH and this is the only component.

Consider now the system represented by the equilibrium.

$$CaCO_3(s)=CaO(s)+CO_2(g)$$

In this system, there are three phases, viz. solid $CaCO_3$, solid CaO and gaseous CO_2 and two components. These two components may be chosen as any two of the substances involved in the equilibrium. If CaO and CO_2 are taken, then the compositions of various phases can be expressed as follows:

$$CaCO_3 : CaO+CO_2$$
$$CaO \quad : CaO+0CO_2$$
$$CO_2 \quad : 0CaO+CO_2$$

The composition of the three phases could be expressed equally by taking $CaCO_3$ and CaO or $CaCO_3$ and CO_2 as the components. Thus we find that the smallest number of constituents by means of which the composition of each phase can be expressed is two and hence, this is a two-component system.

In the same way, it can be shown that the dissociation of any carbonate, oxide or similar compounds involves two components; the same is true for salt hydrate equilibria *e.g.*,

$$CuSO_45H_2O_{(s)}=CuSO_4.3HO_{2(s)}+2H_2O_{(g)}$$

where the simplest components are evidently $CuSO_4$ and H_2O.

Similarly for the equilibrium,

$$Fe(s)+H_2O(g)=FeO(s)+H_2(g)$$

it can be shown that it consists of three components.

Degrees of freedom or variance. *The number of degrees of freedom or variance of a system is the number of variable factors* *such as temperature, pressure or concentration which must be specified in order to define the system completely.*

Consider any system having one phase only, say gaseous phase of water. In order to define completely the state of the system, it is necessary to specify both temperature and pressure. The system, therefore, has two degrees of freedom or it is said to be *bivariant.* When two phases are in equilibrium, say ice and water, only temperature or pressure need be arbitrarily fixed to define the system completely. This system has one degree of freedom or it is *univariant.* If a system has three phases in equilibrium, such as in the water system in which ice, water and water vapor are together present at triple point, then there are no degrees of freedom. The reason for this lies in the fact that three phases can co-exist in equilibrium only at a particular temperature and pressure which are thus automatically fixed. This type of system is said to be *invariant.*

11.3. DETERMINATION OF DEGREES OF FREEDOM WITHOUT THE HELP OF PHASE RULE

Suppose we consider a gaseous system. It has one component and one phase. Applying phase rule, the number of degrees of freedom for such a system is,

$$\begin{aligned} F &= C+2-P \\ &= 1+2-1=2 \end{aligned}$$

But the question is, how we derive $F=2$ in case of one component and one phase without the help of Phase Rule? We know from experience that for every homogeneous phase, there is an equation of state or phase equation which is given by

$$f(P, T, C)=0$$

where P=pressure, T=temperature and C=concentration are three variables in all. In this equation, three variables are connected by one relation. Now if we subtract from the total possible variables, the number of equations of state by which these variables are connected, we get the remainder as the number of degrees of freedom. In this case, there are three variables and one equation of state so that,

$$F=3-1=2$$

Let us now consider a system of one component and two phases *e.g.*, water and water vapor in equilibrium with each other. By applying the phase rule to the system, $F=C+2-P=1+2-2=1$. But how do we actually derive $F=1$?

The approach in this case is almost similar. Here, since there are two phases, therefore, we have two different but unique equations of states for vapor and for liquid. Thus for vapor, we have

$$f_v(P, T, C_v)=0$$

and for water we have

$$f_l(P, T, C_l)=0$$

where C_l and C_v stand for the concentrations of the components in the liquid and vapor phase respectively.

For each of these two phases we have $F=2$.

But for the whole system in which water and water vapors are in equilibrium at a definite temperature and pressure we have got another equation which is chemical potential equation. We know that when two phases are in equilibrium at a constant temperature and pressure, the chemical potential of a given component in the two phases is the same. Thus

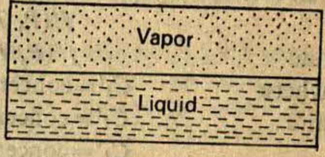


Fig. 11.1. Two-phase equilibria.

$$\mu^l_{H_2O}\,(P, T, C_l)=\mu^v_{H_2O}\,(P, T, C_v).$$

So there are four possible variables—P, T, C_l and C_v and three equations of state *i.e.*,

$$F=4-3=1.$$

For a system of *one* component and *three* phases *e.g.*, water, vapor and ice in equilibrium, we have $F=0$. In this case, since there are three phases, therefore, three equations of state are possible.

For ice phase $f\,(P, T, C_i)=0$

For liquid (H_2O) phase $f\,(P, T, C_l)=0$

and for vapor phase $f\,(P, T, C_v)=0$

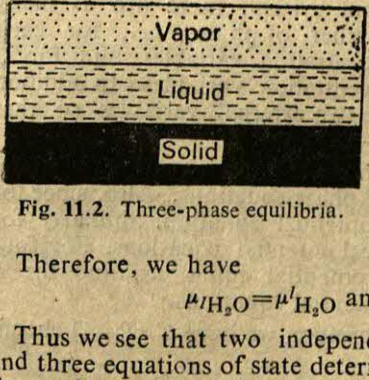


Fig. 11.2. Three-phase equilibria.

where C_i, C_l and C_v stand for the concentration of the component in solid, liquid and vapor form respectively.

When three phases coexist in equilibrium at a definite temperature and pressure, the chemical potential of a given component is same in each phase.

Therefore, we have

$$\mu^i_{H_2O}=\mu^l_{H_2O} \text{ and } \mu^l_{H_2O}=\mu^v_{H_2O}$$

Thus we see that two independent chemical potential equations and three equations of state determine the equilibrium between the three phases. Since the total number of variables is five *i.e.*, P, T, C_i, C_l and C_v,

therefore, $F=5-5=0.$

For a system which consists of a *homogeneous solution of sugar in water, we have an equation of state.*

$$f\,(T, P, C_{H_2O}, C_{sugar})=0$$

where C_{H_2O} and C_{sugar} stand for the concentration of water and sugar respectively, and total number of possible variables$=4$.

Therefore, $F=4-1=3$.

System having two Phases and two Components

In this case, the phase equations are

$$f'(P, T, C_1', C_2')=0$$

and

$$f''(P, T, C_1'', C_2'')=0$$

where C_1'=concentration of component 1 in phase 1.
and C_2'=concentration of component 2 in phase 1.
C_1''=concentration of component 1 in phase 2.
C_2''=concentration of component 2 in phase 2.

Also, chemical potential equation for the 1st component in the two phases is,

$$\mu_1' (P, T, C_1', C_2')=\pi_1'' (P, T, C_1'', C_2'').$$

Similarly, for the second component

$$\mu_2' (P, T, C_1', C_2')=\mu_2'' (P, T, C_1'', C_2'').$$

Now since total number of possible variables$=6$
and total number of equations$=4$.

Hence $F=6-4=2$

11.4. DEDUCTION OF PHASE RULE

Consider a system of P phases and C components. As we have already seen that for a one component system, there are as many concentration variables as the number of phases *i.e.*, for each component, we have got P concentration variables and for C components, we have got $C \times P$ concentration variables. In addition to this, pressure and temperature are two external variables so that in all, *total number of variables* $CP+2$.

Again, since for each phase we have got an equation of state, therefore, for P phases, we have P phase equations. Also, since for two phases, we have one chemical potential equation. Similarly for three phases, we have two chemical potential equations. For four phases, we have three chemical potential equations, and for P phases, we have $(P-1)$ chemical potential equations.

Since there are C components, therefore, we have $C\ (P-1)$ chemical potential equations.

Therefore, total number of equations$=P+C(P-1)$

$\therefore$ F=Total number of variables$-$Total number of equations

$$=CP+2-[P+C(P-1)]$$

$$=CP+2-P-CP+C$$

or $F+P=C+2$

This is the *phase rule* as was deduced by J.W. Gibbs.

It may be noted that if a particular component is absent from any phase, the number of concentration variables is reduced correspondingly. At the same time, there will be a similar decrease in the number of independent equations determined by the equality of chemical potential. The net effect will thus be to leave unchanged the number of degree of freedom.

Suppose, one component is excluded from certain phases. Then the number of possible variables is $[CP+2-1]$.

Again, since the system consists of P phases, there will be P phase equations and also in order that phases coexist, the chemical potential of each component is the same in all the phases so that if one component is excluded from the phases, then $[C(P-1)-1]$ will be chemical potential equations.

$$\therefore \quad F=[CP+2-1]-[P+C(P-1)-1]$$
$$=CP+2-1-P-CP+C+1$$
$$=C+2-P.$$

Limitations of phase rule. The phase rule gives us a very limited information. It only gives the number of degrees of freedom, but does not tell us that by how much and in what direction the system moves to achieve the new set of equilibrium. Suppose, we have any system *e.g.*, ice, liquid and vapor in equilibrium. If we change the temperature, the pressure will also change in order to have new set of equilibrium. But phase rule does not tell us that by how much, the pressure will change and in what direction system be moving.

11.5. APPLICATIONS OF THE PHASE RULE

One Component System

In one component system, $C=1$.

Therefore, from Phase Rule,

$$F=1-P+2$$
$$F=3-P \qquad \ldots (11.1)$$

Since the minimum number of phases which can be possible for any system is one, therefore, it follows from equation (11.1) that maximum value of degree of freedom for a one component system is two as given by

$$F=3-1=2$$

So, in order to define one component system, two variables must be specified. The two variables chosen are temperature and pressure. For a one component system, the concentration variable is not taken into account because the composition is always same.

If two phases coexist in equilibrium with each other, then from equation (11.1), $F=1$ *i.e.*, the system is monovariant and one of the two variables is sufficient to define the system completely.

On the other hand, when three phases are in equilibrium with each other, then $F=0$, *i.e.*, it is not necessary to specify any variable and the system is non-variant (or invariant).

Thus the maximum number of phases which can coexist in equilibrium in one component system is three.

These facts, predicted by the phase rule, can be represented graphically by considering temperature—pressure diagram.

Water System

Water can exist in three possible forms, namely ice (solid), water (liquid) and water vapor. These three forms can lead to the following equilibria:

Two-phase equilibria	Three-phase equilibria.
solid—liquid	
solid—vapor	solid—liquid—vapor.
liquid—vapor	

When phase rule is applied to these possible equilibria, three bivariant single-phase areas, three monovariant two-phase equilibrium lines, and one invariant three-phase equilibrium point are anticipated.

The equilibrium diagram for the water system is shown in the Fig. 11.3.

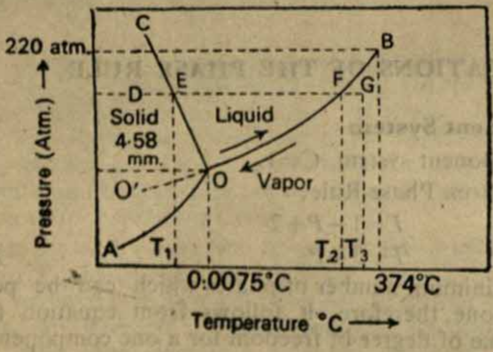


Fig. 11.3. Phase diagram for water system.

The diagram consists of three curves *OA*, *OB*, and *OC* representing the equilibrium conditions between two phases and expressing the fact that along the curves, the system is bivariant. These curves divide the diagram into three areas—*AOB*, *BOC* and *AOC* which are respectively the fields of the existance of vapor, liquid and solid. Within the single phase areas, the system is bivariant. *O* represents the point where the three curves are meeting. At this point, three phases coexist in equilibrium and system is invariant.

The study of the equilibrium diagram involves the discussion of the curves, areas and points. This is done as follows:

The Study of the Curves

(*i*) **Curve OA**. This part separates the solid region from the vapor region and is known as the vapor pressure curve or the sublimation curve of ice, because it gives the vapor pressure of solid ice in equilibrium with water vapor at different temperatures. The curve starts from *O*, the freezing point of water and extends up to absolute zero. As can be seen from the diagram, there is one and only one temperature corresponding to any pressure and vice versa at which the two phases are in equilibrium.

Hence, the degree of freedom is one and the system is univariant as predicted by the phase rule.

$$F=C-P+2$$
$$=1-2+2=1$$

(*ii*) **Curve OB**, This curve separates the liquid region from vapor region and is known as the vapor pressure curve or vaporisation curve of liquid water because it gives the vapor pressure of water in equilibrium with vapors at different temperatures. This curve starts from *O* and extends up to critical temperature (the temperature above which the liquid does not exist). This critical temperature is 374°C and the pressure corresponding to this temperature is 220 atm. It can be clearly seen that corresponding to any particular temperature, there is one and only one pressure and vice versa at which the two phases are in equilibrium. Hence the degree of freedom is one.

(*iii*) **Curve OC**. This curve separates the solid region from the liquid region and is called the freezing point curve, or fusion curve of ice because it tells how the freezing temperature of water or melting temperature of ice varies with pressure in such a way that the two phases are in equilibrium. This curve again starts from *O* and extends up to very high values of pressure. The degree of freedom of this curve is also one because there is one and only one pressure corresponding to any temperature and vice versa at which solid and liquid phases will coexist in equilibrium.

As can be seen from the diagram, this curve slopes towards the pressure axis. This indicates that the melting point of ice is lowered by increase of pressure or ice melts with decrease of volume. This is in accordance with Le-Chatelier principle.

Metastable curve OO′. If the liquid water is carefully supercooled below point *O*, the curve *OO′* is obtained which is just a continuous extension of curve *BO* (Supercooling means the cooling of liquid below the freezing point without the separation of solid). The phases along *OO′* are water and vapor which are in *metastable equilibrium*. Hence the curve is shown by dotted lines. The supercooled liquid is unstable at these temperatures with respect to ice.

So, as soon as the equilibrium is disturbed by adding a small piece of ice, supercooled liquid will be immediately converted into ice. It should also be noted that the curve OO' lies above OA which means that the metastable vapor pressure of the supercooled water is higher than the vapor pressure of ice. The degree of freedom along this metastable curve is also one.

The areas. The diagram is divided into three areas, *AOC*, *AOB* and *BOC*, bounded by the lines and show the regions of ice, vapor and liquid water respectively. Within these single phase areas, the system is bivariant. This means that in order to define completely a point within any of the areas, it is necessary to specify both temperature and pressure. This also follows from the phase rule as shown below:

$$F=C-P+2$$
$$=1-1+2=2$$

The point *O*. We see from the diagram that the three curves *OA*, *OB* and *OC* are intersecting each other at the only point *O*. This is known as the *triple point* and is obviously the point at which the three phases ice, water, and vapor co-exist in equilibrium. The temperature and pressure corresponding to this equilibrium are 0.0075°C and 4.58 mm respectively. It should be noted that three phases can co-exist in equilibrium only under one set of conditions and neither temperature nor pressure can be changed. If any of the two variables is altered even slightly, the equilibrium is shifted and three phases will not exist together. Hence, the system corresponding to this point is invariant and there is no degree of freedom. This is in accordance with the phase rule.

Since $P=3$, $F=1-3+2=0$

The salient features of water system are given in Table 11.1.

TABLE 11.1

Salient features of water system

Curve/Area/ Point	*Name*	*Phases equilibrium*	*Degrees of freedom*
Curve OA	Vapor pressure curve or the sublimation curve of ice	solid ⇌ vapor	1
Curve OB	Vaporisation curve of liquid water	liquid ⇌ vapor	1
Curve OC	Fusion curve	solid ⇌ liquid	1
Curve OO′	Metastable vaporisation curve of liquid water	liquid ⇌ vapor	1
Area AOC	—	solid	2
Area AOB	—	vapor	2
Area BOC	—	liquid	2
Point O	Triple point	solid ⇌ liquid ⇌ vapor	0

Effect of change of the variables (Pressure and Temperature on the system). In order to understand the manner in which equilibrium changes in the system with a change in the variables, consider the following example. Suppose we want to know the behaviour of the system on heating ice at a constant pressure of 1 atmosphere and a certain temperature below T_1, represented by the point *D* in Fig. 11.3 up to temperature T_3, represented by the point *G*. When the temperature is raised slowly at constant pressure, the system moves along the line *DE*. When it reaches *E*, the ice begins to melt and temperature remains constant till fusion is complete. During fusion the system is bivariant because it will have two phases, solid and liquid, in equilibrium with each other. When the whole of the ice is melted, further rise in temperature will make the system move along the line *EF* in the liquid region. Between *E* and *F*, the only change is an increase in the temperature of the liquid. As soon as the point *F* is reached, vaporisation sets in and temperature will remain constant till vaporisation is complete.

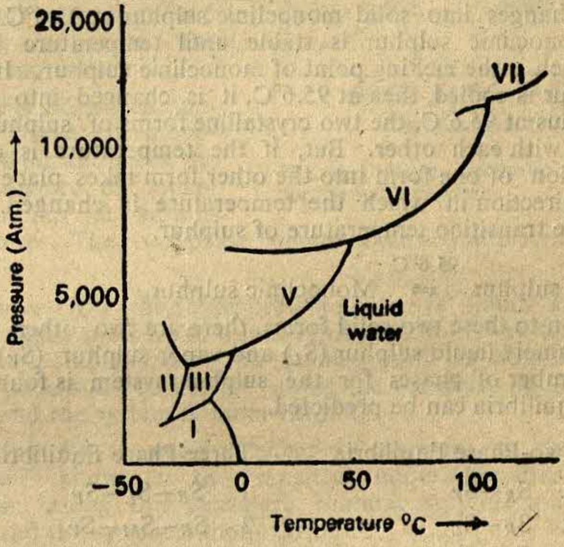


Fig. 11.4. Water system at high pressures.

When the liquid has been completely changed to vapor, then the system will move along *FG* with further rise in temperature in the vapor region. Addition of heat will merely increase the temperature of the vapor until the point *G* is obtained.

In the same manner, we can show how the equilibrium changes in the system with a change in pressure at a constant temperature or with a change in both temperature and pressure.

If water is studied under very high pressures, a number of different forms of ice besides the ordinary form are observed. The various forms differ from the ordinary form in density, crystal structure and other physical properties.

The equilibrium diagram of the system under the conditions of high pressure is as shown in Fig. 11.4. Ice I is ordinary ice, ices II, III, V, VI, VII are the different forms which are stable at very high pressures. Ice IV is the unstable form. There are six triple points as shown in the diagram. It is interesting to note that at very high pressures, melting ice is quite hot. It melts at about 100°C under a pressure of 25,000 atm. The melting point can be raised even up to 190°C if the pressure of 40,000 atm. is achieved.

The Sulphur System

Sulphur exists in two crystalline forms, namely, rhombic (S_R) and monoclinic sulphur (S_M). At ordinary temperatures and under one atmospheric pressure, rhombic sulphur is stable. When heated slowly, it changes into solid monoclinic sulphur at 95.6°C. Above 95.6°C, monoclinic sulphur is stable until temperature 119°C is reached which is the melting point of monoclinic sulphur. If monoclinic sulphur is cooled, then at 95.6°C, it is changed into rhombic sulphur. Thus at 95.6°C, the two crystalline forms of sulphur are in equilibrium with each other. But, if the temperature is changed, transformation of one form into the other form takes place depending on the direction in which the temperature is changed. Hence 95.6°C is the transition temperature of sulphur.

$$\text{Rhombic sulphur} \overset{95.6^\circ\text{C}}{\rightleftharpoons} \text{Monoclinic sulphur.}$$

In addition to these two solid forms, there are two other forms of sulphur—namely liquid sulphur (S_L) and vapor sulphur (S_V). Thus, the total number of phases for the sulphur system is four and the following equilibria can be predicted.

Two-Phase Equilibria	Three-Phase Equilibria
1. S_R-S_V	1. $S_R-S_L-S_V$
2. S_R-S_L	2. $S_R-S_M-S_V$
3. S_R-S_M	3. $S_R-S_M-S_L$
4. S_M-S_V	4. $S_M-S_L-S_V$
5. S_M-S_L	
6. S_L-S_V	

Four-Phase Equilibria

$$S_R-S_M-S_L-S_V$$

When phase rule is applied to four-phase equilibria we find $F=-1$, which is not possible. *So, for a one component system, it is not possible to have four phases existing together in equilibrium.* But, it is possible to have three or any less number of phases together because then the conditions are similar to those holding for the water system.

The schematic equilibrium (or phase) diagram for sulphur system is shown in Fig. 11.5.

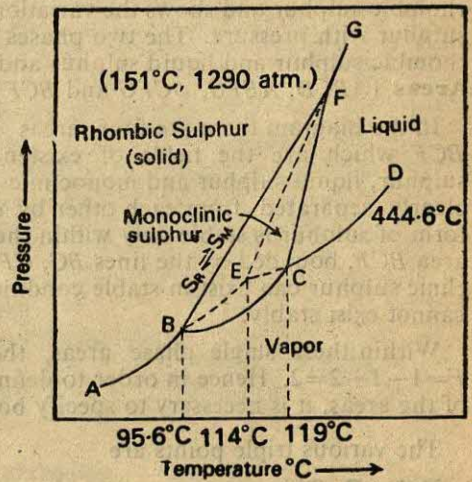


Fig. 11.5. Phase equilibrium diagram for the sulphur system.

The diagram consists of six curves (*AB*, *BC*, *CD*, *BF*, *CF* and *FG*), four areas (*ABCD*, *DCFG*, *ABFG* and *BCF*) and three points (*B*, *C* and *F*).

(*i*) *Curve AB* is the sublimation curve of rhombic sulphur and gives the vapor pressure of rhombic sulphur at various temperatures. The two phases which are in equilibrium along *AB* are rhombic sulphur and the vapor sulphur and the system is monovariant.

(*ii*) *Curve BC* is the sublimation curve of monoclinic sulphur and gives the vapor pressure of monoclinic sulphur at various temperatures. The two phase monovarient equilibrium along *BC* is $S_M \rightleftharpoons S_V$.

(*iii*) *Curve CD* is the vapor pressure curve of liquid sulphur and gives the vapor pressure of liquid sulphur at different temperatures. This curve is stable up to to the boiling point of sulphur 444.6°C. The two phases in equilibrium along the curve are liquid and vapor sulphur and the system is monovariant.

(*iv*) *Curve BF* shows the effect of pressure on the transition point and is known as the transition curve. The two phases in equilibrium along this curve are rhombic sulphur and monoclinic sulphur and the system is monovariant.

(*v*) *Curve CF* represents the variation of the melting point of monoclinic sulphur with pressure and is known as the fusion curve of the monoclinic sulphur. The monovariant equilibrium along *CF* is $S_M \rightleftharpoons S_L$.

It should be noted from the diagram that both the curves *BF* and *CF* slope away from the vertical to the right so that the transition point and melting point of monoclinic sulphur increase with increasing pressure. It follows from Le-Chatelier principle that transition of rhombic sulphur into monoclinic sulphur is accompanied by an increase of volume. Similarly, the conversion of monoclinic sulphur into liquid form is also accompanied by a slight increase of volume.

However, since the transition of rhombic sulphur into monoclinic sulphur is accompanied by a larger increase of volume than the melting of monoclinic sulphur, therefore, the slope of the curve *BF* is much larger than that of *CF* and the two curves meet at the point *F*.

(*vi*) *Curve FG* is known as the *melting point* or *fusion curve* of rhombic sulphur and shows the variation of melting point of rhombic sulphur with pressure. The two phases in equilibrium along *FG* are rhombic sulphur and liquid sulphur and the system is monovariant.

Areas (*ABCD*, *ABFG*, *DCFG* and *BCF*)

In the diagram there are four areas *ABCD*, *ABFG*, *DCFG*, and *BCF* which are the fields of existence of vapor sulphur, rhombic sulphur, liquid sulphur and monoclinic sulphur respectively and are clearly separated from each other by distinct bounding lines. Each form of sulphur is stable only within the specified area. Thus in the area *BCF*, bounded by the lines *BC*, *CF* and *BF*, we find that monoclinic sulphur can exist in stable condition but outside this area it cannot exist stably.

Within these single phase areas, the system is bivariant since $F=1-1+2=2$. Hence in order to define completely a point in any of the areas, it is necessary to specify both the variables.

The various triple points are

Point B. This point represents the transition temperature (95.6°C) at which rhombic sulphur is transformed into monoclinic sulphur. The three phases co-existing in equilibrium at this point are rhombic sulphur, monoclinic sulphur and vapor sulphur.

Point C. This point represents the melting point (119°C) of monoclinic sulphur. The two curves which are intersecting at this point are *BC* and *CD*. Thus the three phases which are in equilibrium with each other at this point are monoclinic sulphur, liquid sulphur and vapor sulphur.

Point F. This point (Temperature=151°C and Pressure=1290 atm), is obtained by the intersection of the curves *BF* and *CF* and corresponds to the equilibrium

$$S_{rhombic} \rightleftharpoons S_{monoclinic} \rightleftharpoons S_{liquid}$$

Since all the triple points represent the exstence of the three phases in equilibrium with each other, therefore

$$F=1-3+2=0$$

i.e., corresponding to each point, the system is invariant and no variable can be altered without disturbing the equilibrium.

Metastable equilibria. Besides the stable equilibria discussed above, there are number of metastable equilibria represented by the dotted lines. If rhombic sulphur is heated rapidly (superheated), it will pass above the transition point *B*, along *BE* without change and finally melt to liquid sulphur at point *E* (Temperature=114°C).

Thus this curve, *BE* which is a continuous extension of *AB*, represents the monovariant metastable equilibria

$$S_R \rightleftharpoons S_V$$

Similarly, the line *CE* which is obtained by supercooling liquid sulphur along the extension of *DC* to *E* represents the monovariant, metastable equilibrium between liquid sulphur and vapor sulphur. Since the two metastable curves *BE* and *CE* are intersecting each other at *E*, this represents the metastable invariant triple point $S_{rhombic}-S_{liquid}-S_{vapor}$

The curve *EF* is the metastable rhombic melting point curve and shows the variation of melting point of metastable rhombic sulphur with pressure. This curve is an extension of the stable *GF* line into the metastable range and the two phases which are in metastable equilibria with each other along this curve are rhombic sulphur and liquid. (Table 11.2).

TABLE 11.2

Salient features of sulphur system

No.	*Curve/Area/ Point*	*Name*	*Phases in equilibrium*	*Degree of freedom*
A. *Stable Equilibria*				
1	Curve AB	Sublimation curve of rhombic sulphur	$S_R \rightleftharpoons S_V$	1
2	Curve BC	Sublimation curve of monoclinic sulphur	$S_M \rightleftharpoons S_V$	1
3	Curve CD	Vaporisation curve of liquid sulphur	$S_L \rightleftharpoons S_V$	1
4	Curve BF	Transition curve	$S_R \rightleftharpoons S_M$	1
5	Curve CF	Fusion curve of monoclinic sulphur	$S_M \rightleftharpoons S_L$	1
6	Curve FG	Fusion curve of rhombic sulphur	$S_R \rightleftharpoons S_L$	1
7	Area ABCD	—	S_V	2
8	Area ABFG	—	S_R	2
9	Area DCFG	—	S_L	2
10	Area BCF	—	S_M	2
11	Point B	Triple point	$S_R \equiv S_M \rightleftharpoons S_V$	0
12	Point C	Triple point	$S_M \rightleftharpoons S_L \rightleftharpoons S_V$	0
13	Point F	Triple point	$S_R \rightleftharpoons S_M \rightleftharpoons S_L$	0
B. *Metastable Equilibria*				
1	Curve BE	Metastable sublimation curve of rhombic sulphur	$S_R \rightleftharpoons S_V$	1
2	Curve CE	Metastable vaporisation curve of liquid sulphur	$S_L \rightleftharpoons S_V$	1
3	Curve CF	Metastable fusion curve of rhombic sulphur	$S_R \rightleftharpoons S_L$	1
4	Point E	Metastable triple point	$S_R \rightleftharpoons S_L \rightleftharpoons S_V$	0

Other one component systems. Of the various other one component systems, some important examples are: the systems phosphorus, carbon, carbon dioxide, benzophenone, helium, etc. These systems can be discussed in the same manner as the water and sulphur systems. One interesting and unique feature of the helium system is that helium exists in two different liquid phases—liquid helium I and liquid helium II and there is no solid-liquid-vapor triple point.

11.6. TWO-COMPONENT SYSTEMS

For a two-component system, $C=2$ and the phase rule equation can be written as

$$F=C-P+2$$

$$=2-P+2=4-P \qquad \ldots (11.2)$$

Since the minimum number of phases for any system is one, therefore from equation (1), it follows that the maximum number of degrees of freedom in a two-component system is

$$F=4-1=3$$

This means that in order to define a two-component system completely, all the three variables—pressure, temperature and concentration must be specified. In order to represent these relations graphically, we require a three dimensional diagram in which three co-ordinate axes representing pressure, temperature and concentration are at right angles to each other. This will lead to a space model which is difficult to construct on paper. In order to remove this difficulty, the common practice is to fix one of the three independent variables *i.e.*, one of the three variables is kept constant. It is then possible to draw a two dimensional plot of any two of the three variables which will graphically represent the conditions of equilibrium for a two-component system.

The various equilibria which can be possible for a two-component system are: (*i*) solid-liquid equilibria, (*ii*) solid-gas equilibria, (*iii*) liquid-liquid equilibria, and (*iv*) liquid-gas equilibria.

We shall be limiting ourselves to the study of only solid-liquid equilibria having no gas phase. Such systems having no gas phase are known as *condensed systems*. Since the effect of pressure is small on this type of equilibria, therefore, experiments are usually conducted under atmospheric pressure, thus keeping the pressure constant. This will reduce the degree of freedom of the system by one, and for such system, the phase-rule becomes

$$F=C-P+1 \qquad \ldots (11.3)$$

This is known as the *reduced phase rule* having two variables, namely temperature and concentration of one of the constituents. Therefore solid-liquid equilibria are represented on temperature-composition diagrams.

Determination of Equilibrium Conditions between Solid and Liquid Phases by Thermal Analysis

The shape of the freezing point curves for any system, especially those involving metals, can be determined experimentally by thermal analysis. This method involves a study of the cooling curves of various compositions of a system during solidification. From such curves, it is possible to obtain the freezing point of the mixture and the eutectic temperature for the system and to detect the temperatures at which various transformations and transitions occur.

In order to understand the experimental steps involved in this procedure, the interpretation of the curves and the plotting of the final diagram, consider a system *AB*. A series of mixtures of known amounts of the two constituents, ranging in overall composition from 100 per cent *A* to 100 per cent *B*, are prepared, and each mixture is heated to a high temperature until it melts to a homogeneous liquid. It is then allowed to cool steadily and the temperature and time readings are taken until the mixture is completely solidified. Finally, the cooling curves are obtained by plotting the temperatures against time. The curves obtained for various compositions are shown schematically in Fig. 11.6.

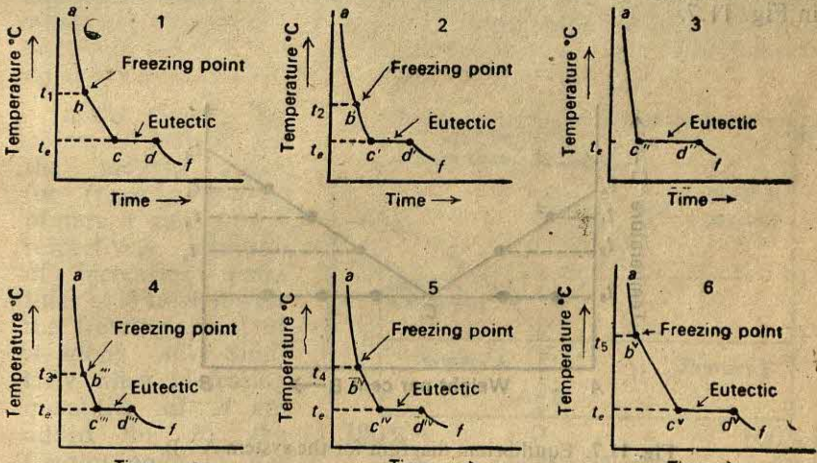


Fig. 11.6. Cooling curves.

In curve (1), the homogeneous liquid cools along the curve *ab*; at *b*, solid *A* commences to separate from the mixture. The separation of solid *A* is accompanied by the evolution of heat, equal in amount but opposite in sign to the heat of fusion. Consequently, the rate of cooling slows and a break in the curve appears at *b*. The temperature t_1 is a point on the liquidus curve for this composition. The cooling continues from *b* to *c* at a slower rate than before; at *c* the eutectic point is attained when the temperature remains constant, along *cd*, until solidification is complete at *d*. The horizontal portion *cd* indicates the coexistence of three phases and is called the *eutectic halt*. When no more liquid is left, cooling of the solid proceeds quickly along the curve *df*. Curve (2) is for a liquid somewhat richer in *B*; the interpretation is the same and t_2 is the point on the liquidus curve. If the liquid mixture coincides exactly with the composition at the eutectic point, the region *bc* will not exist, the cooling curve will then show a break only when the eutectic temperature is reached. This is illustrated in curve 3). Similarly, fourth, fifth and sixth curves represent cooling curves for compositions on the *B*—rich side of the eutectic point. t_4, t_5 and t_6 are the corresponding points on the liquidus curve.

To construct the equilibrium diagram from the cooling curves, the temperatures t_1, t_2, t_3, t_4, t_5 and t_6 are taken off the cooling curves for the various overall compositions and are plotted on a temperature-composition diagram. In order to complete the diagram, it is necessary to know the freezing points (or melting points) of pure *A* and *B* respectively. These temperatures, t_A and t_B, are determined by means of cooling curves, for the pure liquid will solidify at a constant temperature. Smooth curves are then drawn through all the freezing and eutectic temperatures to yield the diagram shown in Fig. 11.7.

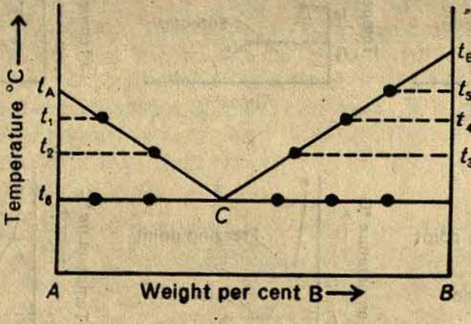


Fig. 11.7. Equilibrium diagram for the system A—B.

In the equilibrium diagram, the two curves are intersecting at the point *C* which represents the eutectic composition.

Classification of Two-Component Solid-liquid Equilibria

Two-component solid-liquid equilibria can be classified into three categories depending on the miscibility of the liquid phases. These categories are further subdivided depending on the nature of the solid phases crystallizing from the solution.

Category one. *The two components are completely miscible with one another in the liquid state.*

Type I. On solidification, only an intimate mixture of the pure components (known as Eutectic) is obtained.

Type II. The two components form a compound with incongruent melting point.

Type III. The two components form a compound with incongruent melting point.

Category two. *The two components are partially miscible with one another in the liquid state.*

Type I. Only an intimate mixture of the pure components crystallises out on solidification.

Category three. *The two components are completely immiscible in the liquid state.*

Type I. Only an intimate mixture of the pure components crystallises out on solidification.

In this Chapter, we shall consider only *Category one.*

Type I. Formation of Simple Eutectic (general diagram)

Let us consider a general case of two-component condensed systems belonging to type I. It consists of two components *A* and *B* which are completely miscible in the liquid state and their solutions yield only pure *A* or pure *B* as solid phases. The temperature—composition curve of such a system is shown in Fig. 11.8.

In the figure, the points *A* and *B* are the melting points (or freezing points) of pure *A* and pure *B* respectively. Addition of increasing quantities of *B* to *A* lowers the freezing point of *A* along *AC*. Similarly when increasing quantities of *A* are added to *B*, the freezing point of *B* is lowered along *BC*.

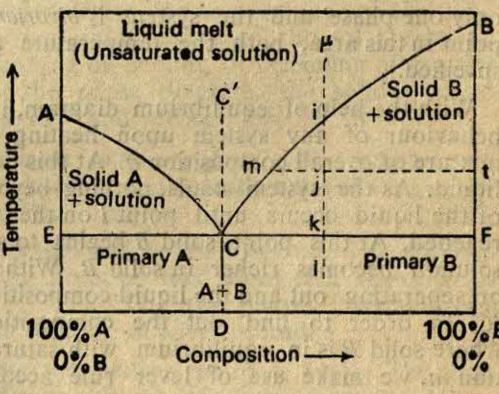


Fig. 11.8. Simple eutectic system.

The curve *AC* is known as the freezing point curve of the component *A* and represents the composition of the solutions saturated with solid *A* at temperatures between *A* and *AC*. Thus we see that the two phases in equilibrium along this curve are solid *A* and solution of *B* in *A*. Similarly, the curve *BC* is known as the freezing point curve of the component *B* and represents the composition of the solution saturated with solid B at temperatures between B and BC. Along this curve, solid B is in equilibrium with solution of A in B.

These two curves represent the two-phase equilibria which are *univarient* as can be seen by applying reduced phase rule equation.

$F=C-P+1=2-2+1=1$ (Since measurements are being made at atmospheric pressure).

These two curves intersect at the point C where both solids A and B are in equilibrium with the liquid phase. Since there are three phases in equilibrium at this point, it is *invarient* in character. This can be easily followed from the reduced phase rule equation

$$F=C-P+1=2-3+1=0.$$

Thus at this point, the temperature and composition of the solution must remain constant as long as three phases co-exist in equilibrium. If any of the two variables is changed, at least one of the phases will disappear. Moreover, as can be seen from the diagram, the point C is the lowest temperature at which any liquid mixture can exist. Below this point, the system is completely solidified. Point C is known as the *Eutectic Point*. Temperature corresponding to this point is known as the *Eutectic Temperature* and the composition corresponding to this point is known as the *Eutectic Composition*.

The area above the lines AC and BC is the field of existence of unsaturated solution or liquid melt. In this area, the two components are present as a homogeneous liquid solution. Thus there is only one phase and the system is *bivariant*. In order to define any point in this area, both the temperature and composition must be specified.

With the help of equilibrium diagram, it is possible at predict the behaviour of any system upon heating or cooling. Consider a mixture of overall composition h. At this point, the system is entirely liquid. As the system cools, nothing beyond a drop of temperature of the liquid occurs until point i on the freezing point curve BC is reached. At this point, solid B begins to separate and the saturated solution becomes richer in solid B. With further cooling, B keeps on separating out and the liquid composition moves along the curve iC. In order to find out the composition at any temperature t, where solid B is in equilibrium with saturated solution of composition m, we make use of lever rule according to which the ratio $\frac{jm}{jt}$ is the relative amount of solid B to liquid mixture. As cooling continues till the eutectic temperature is reached, point k is obtained. At this point, solid A begins to separate in addition to B. The temperature now remains constant until all the liquid solidifies. On complete solidification, further decrease in temperature will cause the decrease in temperature of the mixed solids along the line kl. If the process is done in reverse, that is solid l is heated until it liquefies completely about i, the changes described above take place exactly in the reverse order.

(The constant composition line *hijkl* is known as isopleth.)

In the same manner, we can explain the behaviour of the system on the left hand side of the figure.

Let us now consider a special case in which the composition of the liquid C' is exactly same as that of the eutectic (Point C). In this case, nothing beyond a drop of temperature of the liquid occurs until the eutectic temperature is reached at C. At this temperature, both the solids A and B will begin to separate simultaneously, and the temperature will remain constant until whole of the liquid is solidified.

Microscopic examination of the eutectic mixture has revealed the fact that it consists of fine crystals of A and B. Hence an eutectic is a mixture and not a compound. On the left hand side of the line CD, there are relatively large crystals of A and an intimate mixture of finer crystals of A and B which crystallise in definite composition corresponding to point C. The larger crystals are called *primary crystals*. Similarly on the right hand side, we have solid B as primary crystals.

Solidus and liquidus curves. A liquidus curve is the temperature composition curve of the liquid phase and gives the composition of the solid in equilibrium with the liquid phase. It is, therefore, the freezing point curve. It corresponds to the beginning of freezing. In the phase diagram, the liquidus curves are AC and BC.

The solidus curve which indicates the composition of the solid phase is the temperature-composition curve of the solid mixture. It corresponds to end of freezing on cooling or beginning of melting on heating the system. In the phase diagram, the solidus curves comprise the horizontal line ECF and vertical lines EA and FB.

The most important example of this type of system is the Lead-Silver System. The equilibrium diagram is exactly same as the general diagram and is as shown in Fig. 11.9.

Point A (327°C) represents the melting point of lead. The addition of silver lowers the freezing point of lead along AC. Hence AC is the freezing point curve of lead. The two phases in equilibrium along AC are solid lead and solution of silver in lead.

Point B (961°C) represents the melting point of silver. The addition of lead lowers the freezing point of silver along BC. Hence BC is the freezing point curve of silver. The two phases in equilibrium along BC are solid silver and solution of lead in silver. As the two curves represent the two phase equilibria, they are *univariant*.

The two curves intersect at the eutectic point C. Here, both solids (silver and lead) are in equilibrium with each other. As there are three phases in equilibrium at the eutectic point, it is *univariant*.

Eutectic temperature is 303°C and eutectic composition is 2.6 per cent of silver and 97.4 per cent of lead.

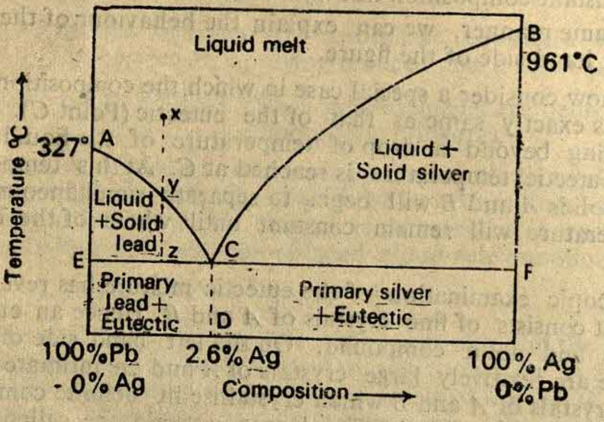


Fig. 11.9. Lead-silver system.

Pattinson's process of desilverisation of lead. It is based on the equilibrium diagram of lead-silver system. We know that argentiferrous lead contains very small amount of silver (0·1 per cent of silver). In order to enrich this ore with silver, it is heated to a high temperature in order to get the liquid melt. It is then allowed to cool. The temperature of the melt will fall along *xy*. At *y*, separation of lead begins to take place. If cooling is continued further, the equilibrium will shift along *yC*. Solid lead will keep on separating and the resulting solution becomes richer and richer in silver until point *C* is reached and the composition of silver rises to 2.6 per cent. Solid lead is removed by ladels. Thus we see that the original argentiferrous lead which contained 0.1 per cent of silver now contains 2.6 per cent of the metal. Some other examples of two-component systems with simple eutectic are given below in Table 11.3.

TABLE 11.3

A	*Melting point*	*B*	*Melting point*	*Eutectic temperature*
Lead	327°C	Antimony	630°C	246°C
Bismuth	268°C	Cadmium	313°C	146°C
Aluminium	657°C	Silicon	1412°C	578°C
Silver chloride	451°C	Potassium chloride	790°C	306°C
Methyl chloride	−63.5°C	Benzene	5.4°C	−79°C

Other simple eutectic systems involving salt and water. The phase diagram of systems involving salt and water are almost similar to the phase diagram of simple eutectic systems involving two metals or two salts. The only fundamental difference is that with salt-water system, the melting point of the salt in the equilibrium diagram cannot be realised. This is due to the fact that the melting point of the salt is generally much higher than the critical temperature of the water in the solution.

The equilibrium diagram for potassium iodide-water system is shown in Fig. 11.10.

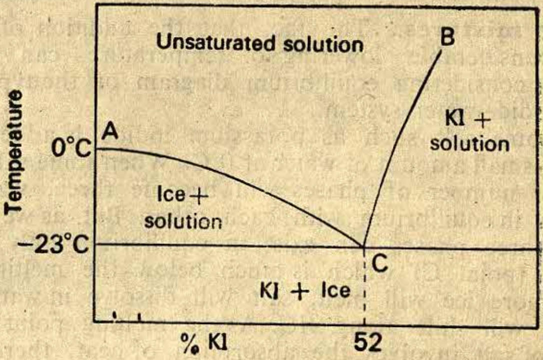


Fig. 11.10. Potassium iodide-water system.

As can be seen, there is much resemblance between this diagram and the general diagram of binary systems forming eutectic although the melting point of potassium iodide, at the extreme right, is not attained due to the reason explained above.

Point *A* is the melting point of ice (or freezing point of water). As increasing quantity of potassium iodide is added, the freezing point of water gets lowered and the curve *AC* is realised. This curve is known as the freezing point curve of water (or fusion curve of ice). Along *AC*, ice separates from potassium iodide solution and the system is monovariant.

Similarly, *BC* is the *monovariant solubility curve* of potassium iodide. Along this curve, solid *KI* is in equilibrium with the solution. The steep rise of the curve shows that this solubility of potassium iodide increases slowly with the temperature.

The two curves are intersecting at the point *C*(−23°C). At this point, there are three phases: ice, potassium iodide and solution, in equilibrium with each other. Hence it is the non-variant eutectic point or cryohydric point of the system. It gives the lowest temperature at which an aqueous solution of potassium iodide can exist at atmospheric pressure. All solutions on cooling will ultimately show a halt in temperature at this point until the liquid phase has solidified. Similarly, a solid mixture of the same composition as the eutectic mixture, on heating melts sharply at this point. The salt-water mixture deposits at this point was therefore considered to be a definite compound (salt hydrate) at one time. This was given the name cryohydrate.

However, on closer examination, it was found that the physical properties, such as heat of solution and density of the eutectic solid, are equal to the mean values of the two components. The heterogeneous structure of the solid eutectic was also observed under a microscope. This suggests, therefore, that the solid separating at this eutectic point is a mixture and not the *so called compound.*

Freezing mixtures. The fact that the addition of salt to ice results in considerable lowering of temperature can be readily explained by considering equilibrium diagram of the type as in the potassium iodide-water system.

Suppose some salt such as potassium iodide is added to ice in contact with small amount of water at 0°C. When some salt dissolves in water, the number of phases will become three, viz., salt, ice and solution in equilibrium with each other. But as we have seen above that three phases can exist in equilibrium only at eutectic temperature (point C) which is much below the melting point of ice, hence more ice will melt, salt will dissolve in water and the composition will shift along *AC*. As the melting point of ice and dissolution of salt involves the absorption of heat, therefore, temperature of the system will fall (if there is no external source of heat) along *AC*. This will go on till the eutectic temperature is reached provided salt is added as fast as it dissolves. Similarly, eutectic temperature can be attained by adding ice to the system salt-solution, (curve *BC*). Eutectic temperature is the lowest temperature that can be attained for any system and is different for different systems.

Type II. Formation of Compound with Congruent Melting Point

A compound is said to possess congruent melting point if it melts sharply at a constant temperature into liquid having the same composition as that of the solid.

Let us consider a general case in which the two substances *A* and *B* form a stable solid compound *AB* having a congruent melting point. The phase diagram for this type of system is as shown in Fig. 11.11.

The diagram may be thought of as being composed of two simple eutectic diagrams—one for *A—AB* and the other for *AB—B*, joined at the position of the arrows as shown in the figure. Each position can now be discussed in the same manner as was done for type I.

In the composite diagram, there are two eutectics, one of *AB—A* —Liquid (Point *C*) and the other of *AB—B*—Liquid (Point *E*). The maximum (Point *D*) in the diagram is the melting point of the compound *AB*. This is called as the congruent melting point of the compound because the solid and liquid phases of the compound at this point have the same composition. It should be noted that at the temperature corresponding to *D*, the two component system becomes

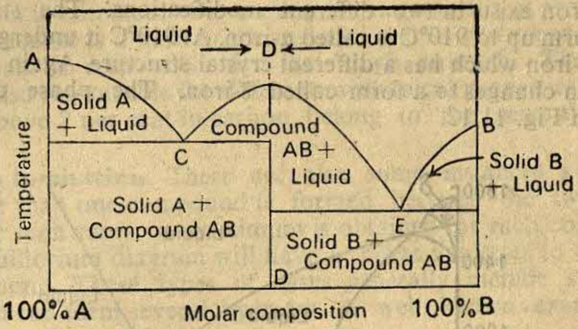


Fig. 11.11. Formation of compound with congruent melting point.

a one component system because both the solid and liquid phases contain the same compound *AB*. Therefore, it is a non-variant point as can be seen from the phase rule.

$$F=1-2+1=0$$

The point *D*, therefore, represents a definite temperature just as the melting points of pure components *A* and *B*. Generally, it has been observed that the melting point of the compound lies above the melting points of the two components, *A* and *B*. However, it is not so always. There are number of examples known in which the melting point of the compound lies below or between the melting points of the two single components. It should also be borne out in mind that in such cases, on cooling a melt of any composition between the two eutectic compositions, the first solid to be deposited is always the compound.

Some examples of two-component systems in which solid compounds are formed are given in Table 11.4.

TABLE 11.4

A	*Melting point*	*B*	*Melting point*	*Compound*	*M.P.*
Aluminium	657°C	Magnesium	650°C	Al_3Mg_4	463
Calcium chloride	777°C	Potassium chloride	790°C	$CaCl_2$-KCl	754
Gold	1064°C	Tin	232°C	Au-Sn	425
Zinc	420°C	Magnesium	650°C	Mg-Zn_2	590
Diphenylamine	52.8°C	Benzophenone	47.7°C	AB	4.02
Aluminium	657°C	Selenium	217°C	Al_2Se_2	—
Gold	1064°C	Tellurium	450°C	$AuTe_2$	—

The Iron-Corbon System

The iron-carbon system is the backbone of ferrous metallurgy. The part of the phase diagram which is of importance extends from pure iron to the compound iron-carbide, or cementite, Fe_3C.

Pure iron exists in two different modifications. The stable crystalline form up to 910°C is called α-iron. At 910°C it undergoes transition to γ-iron which has a different crystal structure. Again at 1401°C, the γ-iron changes to a form called δ-iron. The phase diagram is shown in Fig. 11.12.

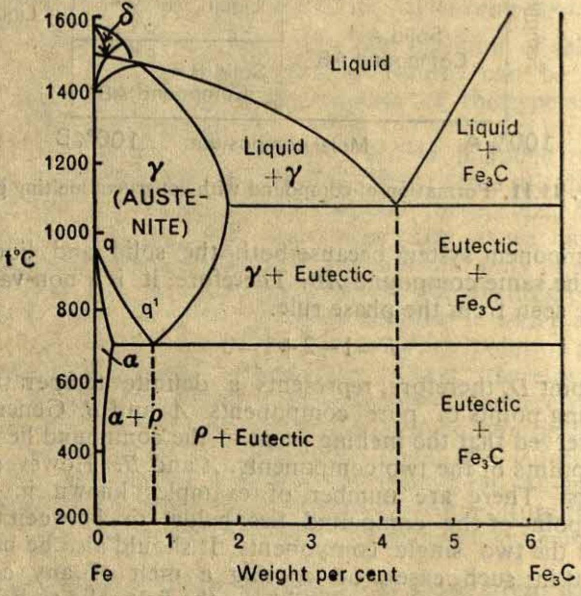


Fig. 11.12. Iron-Carbon System.

The curve *qq'* shows how the transformation temperature of α to γ ferrite is lowered by the intersitial solution of carbon in the iron. The region labelled α-ferrite represents the range of solid solutions of carbon in α-iron. The region γ represents solid solutions of *C* in γ iron. These are given a special name austenite. The decrease in the transition temperature α → γ is terminated at *q'* where the curve intersects the solid solubility curve *rq'* of carbon in γ iron. A point such as *q'* which has the properties of a eutectic but occurs in a completely solid region is called a eutectoid. The two phases formed by the eutectoid decomposition of austenite are α ferrite and cementite. These phases lead to the formation of a structure called pearlite. In case the composition is close to the eutectoid, the steel is composed entirely of pearlite. However, if the composition is richer in carbon or hypereutectoid, it may contain other grains of cementite in addition to those occurring in pearlite. If the hypereutectoid steel is cooled slowly, it may contain additional grains of ferrite. The first stage in the formation seems to be nucleation of a crystallite of cementite. It can be seen from the phase diagram that any composition in below 2 per cent carbon can be heated until a homogeneous solid solution is obtained. On cooling the segregation of two phases occurs. Cementite is a hard brittle material and its occurrence in the pearlitic steels is responsible for their high strength. The rate of cooling is also responsible for different mechanical properties. Compositions above 2 per cent in carbon belong to the general class of cast iron.

Hydrate formation. There are also some instances known in which more than one compound is formed between the two substances. For such cases, a maximum is obtained for each compound and the equilibrium diagram will have a curve analogus to *CDE* for each compound. These types of cases generally include salts and water which can form several hydrates. A well known example of this type is the ferric chloride-water system.

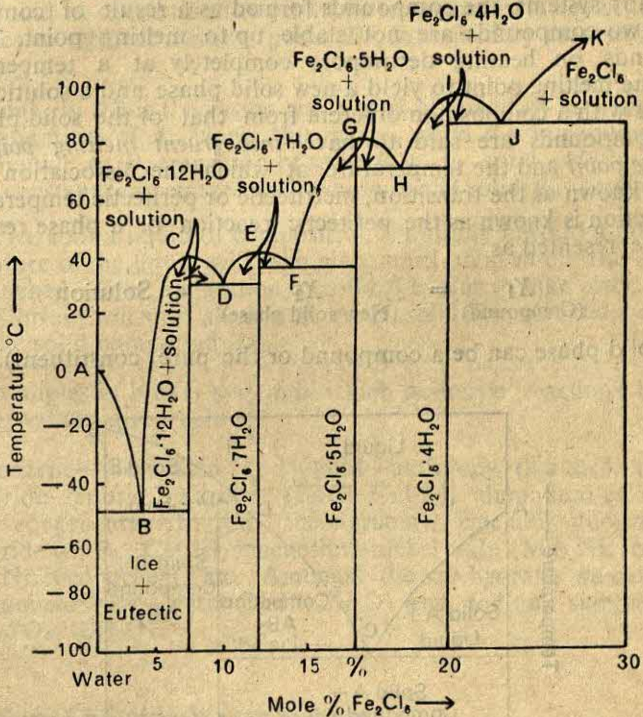


Fig. 11.13. Ferric chloride-water system.

In this system, four stable compounds (hydrates) with congruent melting points have been observed. These are:

(*i*) Do-decahydrate	—$Fe_2Cl_6.12H_2O$
(*ii*) Hepta-hydrate	—$Fe_2Cl_6.7H_2O$
(*iii*) Penta-hydrate	—$Fe_2Cl_6.5H_2O$
(*iv*) Tetra-hydrate	—$Fe_2Cl_6.4H_2O$

(Double molecules of ferric chloride are taken to avoid fractional number of molecules of water in the case of hepta and penta-hydrate.)

The phase diagram shown in Fig. 11.13 can be split in the five simple eutectic diagrams.

In the diagram, the maximum (points *C*, *E*, *G*, *I*) represent the congruent melting points of the various hydrates of Fe_2Cl_6 and the minimum (points *B*, *D*, *F*, *H*, *J*) represent eutectic points.

Type III. Formation of Compound with Incongruent Melting Point

In many systems, the compounds formed as a result of combination of two compounds are not stable up to melting point. These compounds on heating decompose completely at a temperature below the melting point to yield a new solid phase and a solution of the solid with a composition different from that of the solid phases. Such compounds are said to have *incongruent melting point* or *peritectic point* and the temperature at which the dissociation takes place is known as the transition, metritectic or peritectic temperature. The reaction is known as the peritectic reaction or a phase reaction and is represented as

$$\underset{\text{(Compound)}}{X_1} = \underset{\text{(New solid phase)}}{X_2} + \text{Solution}$$

(New solid phase can be a compound or the pure constituent). Let

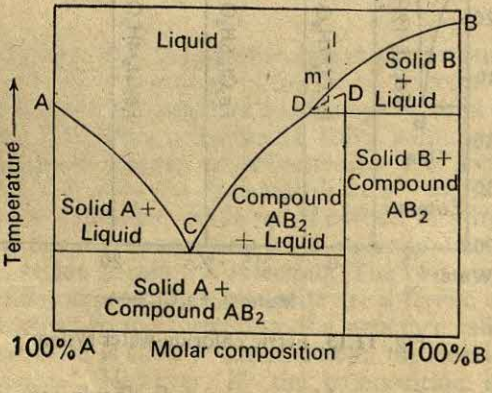


Fig. 11.14. Formation of compound with incongruent melting point.

us consider a general case in which the two components *A* and *B* combine to form a compound AB_2, having incongruent melting point. The phase diagram for this type of behaviour is as shown in Fig. 11.14.

Points *A* and *B* represent the melting points of the pure components *A* and *B*. *AC* is the fusion curve of *A* obtained by adding increasing quantities of *B*. Along this curve, solid *A* is in equilibrium with the liquid. At *C*, in addition to solid *A*, separation of a new solid phase AB_2 also begins to take place. Point *C*, therefore, is the eutectic point of the system. The three phases which are in equilibrium at this point are solid *A*, solid AB_2 and solution. With further addition of *B*, the curve *CD* is traced out. This is known as the fusion curve of AB_2. Along this curve, solid AB_2 is in equilibrium with the liquid phase. At *D*, the compound AB_2 dissociates completely into solid *B* and a solution of composition *D* as given below:

$$\underset{\text{(Compound)}}{AB_2} = \underset{\text{(New solid)}}{B} + \text{Solution}$$

Point *D*, therefore, represents the peritectic point and is invariant. It should be noted that the peritectic temperature is below the hypothetical congruent melting point D' (obtained by extension of curve *CD*).

Similarly *BD* is the fusion curve of *B* obtained by adding increasing quantities of *A*. Along this curve, solid *B* is in equilibrium with the liquid. At *D*, transition of solid *B* in to solid AB_2 takes place at a constant temperature until whole of the solid *B* is consumed.

If we cool a liquid of composition *l*, nothing beyond a fall in temperature of the liquid will take place until point *m* on the curve *BD* is reached. At *m*, separation of solid *B* begins to take place and the equilibrium will shift along *mD*. At *D*, solid *B* is completely replaced by the solid compound AB_2.

Examples of binary system in which peritectic reactions have been observed are given below:

Benzene—picric acid (1 : 1), gold—antimony (Au Sb_2), potassium chloride—cupric chloride (2KCl $CuCl_2$), aluminium-calcium (Al_2 Ca, congruent; Al_3, Ca, incongruent), calcium fluoride-calcium chloride ($CaF_2 : CaCl_2$), magnesium-nickel salt (Mg_2 Ni, congruent; Mg Ni; incongruent) etc. Amongst the salt hydrates we can mention sodium chloride—water ($NaCl.\ 2H_2O$) and sodium sulphate—water ($Na_2SO_4.\ 10H_2O$).

Sodium Chloride-Water System

Sodium chloride with water forms only one hydrate, viz., $NaCl.\ 2H_2O$ having incongruent melting point. The phase diagram for this system is shown in Fig. 11.15.

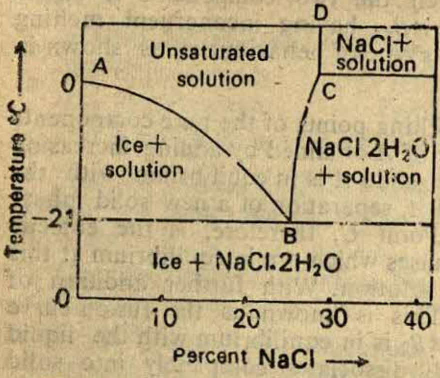


Fig.11.15. Sodium chloride water system.

Point *A* represents the freezing point of water. As more of sodium chloride is added, the freezing point of water gets lowered and the curve *AB* is traced out. This curve is known as the freezing point curve of water. Along this curve the two phases in equilibrium are ice and solution and the system is univariant. At the point *B* (Temperature —21°C and Composition 23% NaCl), in addition to ice, dihydrate of sodium chloride also starts separating out. It is eutectic or cryohydric point of the system. As there are three phases (ice, $NaCl.2H_2O$ and solution) in equilibrium at this point, it is invariant as follows from the condensed phase rule equation.

$$F=C-P+1$$
$$=2-3+1=0.$$

With further addition of sodium chloride and heating, ice disappears and curve *BC* is traced out. Along this curve, solid dihydrate is in equilibrium with the solution. This is known as the solubility curve of dihydrate and is univariant.

This curve extends to the point *C* (0.15°C) where dihydrate decomposes into the new solid (anhydrous sodium chloride) according to the equation.

$$NaCl.2H_2O=NaCl+\text{Solution}$$

The point *C*, therefore, represents the incongruent melting point of the system and is invariant. When whole of the dihydrate has decomposed according to the peritectic reaction shown above, the curve *CD* is traced out. This is the solubility curve of anhydrous sodium chloride and is univariant because along this curve, anhydrous sodium chloride is in equilibrium with the solution.

Sodium Sulphate-Water System

The sodium sulphate—water system forms two incongruent melting compounds, viz.

(*i*) Decahydrate—$Na_2SO_4.10H_2O$ and

(*ii*) Heptahydrate—$Na_2SO_4.7H_2O$ (metastable)

Sodium sulphate can also exist in two enantiotropic crystalline forms, namely rhombic and monoclinic. The phase diagram for this system is as shown in Fig. 11.16.

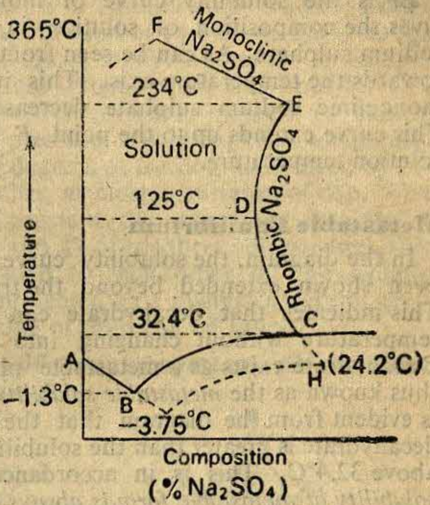


Fig. 11.16. Sodium sulphate-water system.

Point *A* represents the freezing point of water. As increasing quantities of sodium sulphate are added, the freezing point of water is lowered and the curve *AB* is traced out. The curve *AB* is known as the fusion curve of ice and is univariant. Along this, ice is in equilibrium with the solution of sodium sulphate. At the point *B*(−1.3°C), a new solid phase—decahydrate of sodium sulphate—also begins to separate out. This is the eutectic or cryohydric point of this system and is invariant. The three phases in equilibrium at this point are ice, $Na_2SO_4.10H_2O$ and solution.

With further addition of sodium sulphate and heating, ice disappears and the curve *BC* is traced out. Along this curve, solid $Na_2SO_4.10H_2O$ is in equilibrium with the solution and is thus regarded as the *solubility curve* of the decahydrate.

At this point *C* (32.4°C), the decahydrate decomposes into the anhydrous salt (rhombic Na_2SO_4) and solution according to the equation.

$$Na_2SO_4\ 10H_2O \quad = \quad \underset{\text{(Rhombic)}}{Na_2SO_4} \quad + \quad \text{Solution}$$

This is the incongruent melting point or transition point of the decahydrate and the condensed system is invariant.

When whole of the decahydrate has been decomposed into anhydrous rhombic sodium sulphate, the curve *CDE* is traced out with continued heating. This curve gives the composition of solution in equilibrium with anhydrous rhombic sodium sulphate and hence is its solubility curve. The nature of the curve indicates that with increasing temperature, solubility first decreases, passes through a minimum (point *D*, temperature 125°C) and then begins to increase up to *E*.

At the point *E* (234°C), transformation of rhombic sodium sulphate into the monoclinic form takes place At this point, there are two solid phases (rhombic Na_2SO_4 and monoclinic Na_2SO_4) in equilibrium with the solution and the system is invariant.

EF is the solubility curve of monoclinic sodium sulphate and gives the composition of solution in equilibrium with monoclinic sodium sulphate. As can be seen from the diagram, this curve slopes towards the temperature axis. This indicates that the solubility of monoclinic sodium sulphate decreases with increasing temperature. This curve extends up to the point *F* (365°C) which is the critical solution temperature.

Metastable Equilibrium

In the diagram, the solubility curve *BC* of the decahydrate has been shown extended beyond the transition temperature up to *C′*. This indicates that decahydrate can exist even beyond transition temperature without changing into anhydrous sodium sulphate. Decahydrate exists as a metastable phase along *CC′*. This curve is thus known as the *metastable solubility curve* of the decahydrate. It is evident from the diagram that the solubility of the metastable decahydrate is greater than the solubility of anhydrous rhombic salt above 32.4°C. This is in accordance with the general rule that the *solubility of metastable form is always more than that of the stable form at the same temperature.*

The solubility curve *EDC* of the anhydrous rhombic sodium sulphate can also be extended up to *H* without the separation of decahydrate at the point *C* by cooling quickly the saturated solution of anhydrous rhombic sulphate from above the transition temperature. *CH* is, therefore, the *metastable solubility curve of the anhydrous rhombic sodium sulphate.*

In the same manner, the fusion curve *AB* of ice can be extended up to *G*, without the deposition of the decahydrate at the point *B*. *BG* is thus the metastable solubility curve of ice. At the point *G* (−3.75°C), hepta-hydrate $Na_2SO_4.7H_2O$ separates and it represents the *metastable eutectic point.* Under these circumstances, the metastable solubility curve *GH* of the heptahydrate can be realised. Point *H* (24.2°C) represents the metastable transition point at which the heptahydrate decomposes into anhydrous salt.

It should be remembered that heptahydrate is always metastable with respect to the decahydrate and can be formed only if the latter is totally absent. As soon as a small crystal of decahydrate is added, the concentration will fall from *GH* to *BC*.

11.7. THREE-COMPONENT SYSTEMS

According to phase rule, the degree of freedom in a system of three components is given by:

$$F=C-P+2$$
$$F=3-P+2=5-P$$

Since the minimum number of phases that can exist in any system is one, the maximum number of freedom is four. Hence in order to completely define such a system, four variables are required namely, temperature, pressure and concentration of two of the three components. This will require a three dimensional diagram for a complete graphical representation of these systems which is not possible. For this reason, it is customary to represent ternary systems at constant temperature and at constant pressure. By fixing the temperature and pressure, the number of degrees of freedom is reduced by two, so that $F=3-P$ and a system has, at most, a variance of two. When temperature and pressure are constant, the remaining variables are concentration variables X_1, X_2 and X_3 of the three components. These concentration variables are related to each other by the equation $X_1+X_2+X_3=1$ and can be represented on a planner diagram. If we know any two of them, the value of third can be found.

Graphical representation of ternary systems. Of the various methods for plotting two dimensional equilibrium diagrams for ternary systems, the method of Stokes and Roozeboom is very popular and most generally employed. In this method, the variation in concentrations of the three component mixtures at constant temperature and pressure are expressed by means of an equilateral triangle such as that shown in Fig. 11.17.

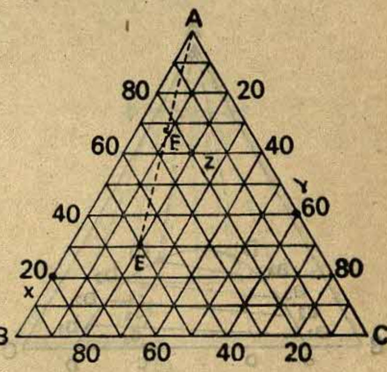


Fig. 11.17. Graphical representation of ternary systems.

Each apex of the triangle represents pure component *i.e.*, 100 per cent of the component with which it is designated. Each side is divided into 10 equal parts and the lines parallel to *BC*, *CA* and *AB* are drawn. Each of the lines parallel to *BC*, *CA* and *AB* represent various percentages of *A*, *B* and *C* respectively. Any point on any side of the triangle refers to a binary system and gives various proportions of constituents in a two-component system while any point within the triangle represents a ternary system and gives various proportions of any mixture composed of *A*, *B* and *C*. Thus a point *X* on the line *AB* represents a two-component systems of 20 per cent *A* and 80 per cent *B*. Similarly, a point *Y* on the line *AC* represents a two-component system of 40 per cent *A* and 60 per cent *C*. Any point *Z* within the triangle represents a ternary system 20 per cent *C*, 20 per cent *B* and 60 per cent *A*. Another important property of this diagram is:

"Any point *F* on the line *AE* represents a mixture that will contain *A* and *E* in the length ratios *EF*: *AF* by weight, if weight percentage is plotted; or by moles, if mole percentage is plotted."

Three-component liquid systems showing partial misci-

bility. Systems composed of three liquids showing partial miscibility may belong to any one of the following three categories:

Type I: Formation of one pair of partially miscible liquids.
Type II: Formation of two pairs of partially miscible liquids.
Type III: Formation of three pairs of partially miscible liquids.

Type I. Formation of One Pair of Partially Miscible Liquids

Consider the behaviour of a three-component liquid system *A-B-C* in which the pairs *A-B* and *A-C* are completely miscible while the pair *B-C* is partially miscible in each other at a given temperature and pressure. On mixing relative amounts of *B* and *C* and thoroughly shaking together, two layers will be obtained, one composed of a solution of *C* in *B*, the other of *B* in *C*. Let the compositions of the two layers be represented by the points *a* and *b* respectively and the overall composition of the system by *c*. When a small amount of *A* is added to the two-layer mixture, it will distribute itself between the two liquid layers and thereby increase the miscibility of *B* and *C*. The increase in miscibility brought about by adding *A* depends upon the amount of *A* added and on the amounts of *B* and *C* present. When enough *A* is added to the system, the composition of the two layers changes to a_1 and b_1 and the overall composition moves along the line *Ac* to the point c_1.

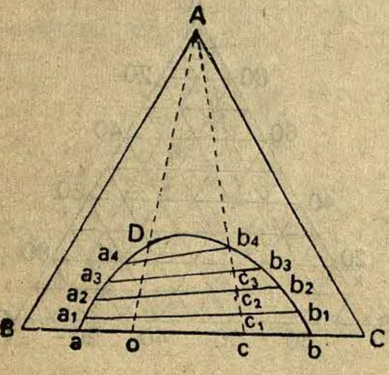


Fig. 11.18. System with one partially miscible pair.

The straight line a_1b_1 through c_1 connects the compositions of the two layers in equilibrium, and is called a *tie-line*. In a similar manner, continued addition of *A* moves the compositions to a_2 b_2 and a_3b_3 and the overall composition moves to c_2 and c_3 along the dashed line. *C*-rich layer grows in size while *B* rich layer diminishes. Finally, at point b_4, only a trace of *B*-rich layer remains and thereafter, only a single solution is obtained.

Since the tie-lines are not parallel, the point at which the compositions of the two layers become identical and the two solutions coalesce into a single liquid phase does not lie at the top of the curve drawn through the series of miscibility points but off to one side at the point *D*. Point *D* is known either as *isothermal critical point* of the system or the *plait point* and can be obtained only by adding *A* to a single mixture of *B* and *C*, with overall composition *o*. See Fig. 11.18.

It follows from the above discussion that any mixture of *A*, *B* and *C* of overall compositions falling within the dome-shaped area will yield two liquid layers of compositions given by the appropriate tie-line through the composition of the mixture. On the other hand, any mixture in the region outside the dome-shaped area will represent a homogeneous solution of the three liquids. The curve *aDb* is frequently called a *binodal curve*.

Examples. Systems such as acetic acid-chloroform-water and acetone-water-phenol belong to this category.

Type II. Formation of Two Pairs of Partially Miscible Liquids

Consider a system of three liquids *A-B-C* in which the pairs *A-B* and *A-C* are partially miscible, while the pair *B-C* is completely miscible. Such a system will exhibit two binodal curves as shown in Fig. 11.19 (a).

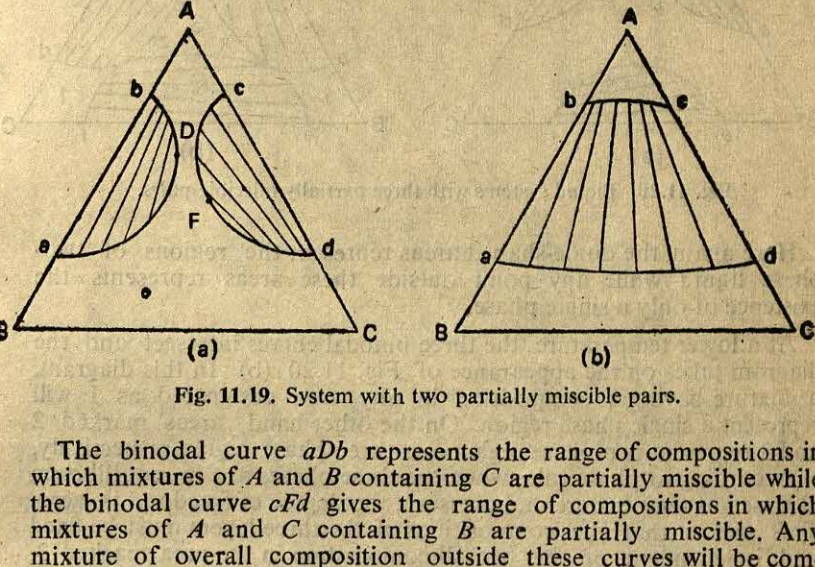


Fig. 11.19. System with two partially miscible pairs.

The binodal curve *aDb* represents the range of compositions in which mixtures of *A* and *B* containing *C* are partially miscible while the binodal curve *cFd* gives the range of compositions in which mixtures of *A* and *C* containing *B* are partially miscible. Any mixture of overall composition outside these curves will be completely miscible. The two points *D* and *F* are the respective plait points of the two heterogeneous systems. The tie-lines in the two curves show the compositions of the various layers in equilibrium.

In certain cases, it has been observed that the two binodal curves in Fig. 11.19 (a) may intersect each other on lowering the temperature. This will lead to the formation of the 'band' *abcd* across the two phase regions in the diagram as shown in Fig. 11.19 (b). *ad* and *bc* give the compositions of the two layers respectively and the indicated tie-lines join various solutions in equilibrium.

Examples. System such as succinic nitrile-water-ethyl alcohol between 18.5°C and 31°C belongs to type showing no band formation while systems such as water-phenol-aniline and water-ethyl acetate-*n*-butyl alcohol show the formation of 'band.'

Type III. Formation of Three Pairs of Partially Miscible Liquids

Consider a system in which all the three liquids are partially miscible. Such a system will exhibit three binodal curves as shown in Fig. 11.20 (a).

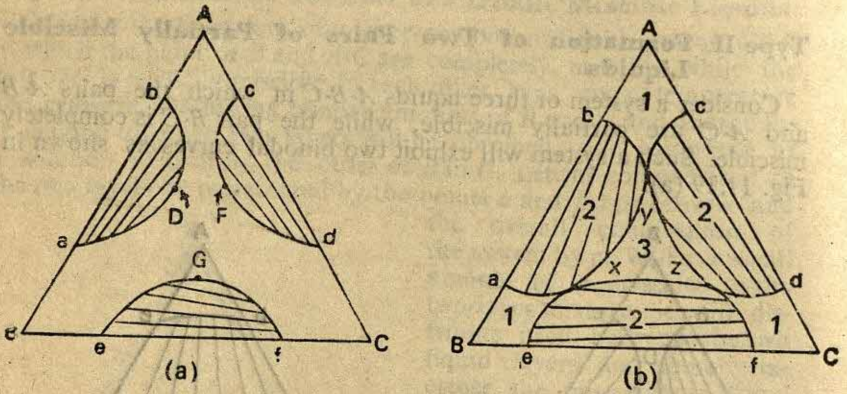


Fig. 11.20. Liquid systems with three partially miscible pairs.

Here again the dome-shaped areas represent the regions of two-phase liquid while any point outside these areas represents the existence of only a single phase.

At a lower temperature, the three binodal curves intersect and the diagram takes on the appearance of Fig. 11.20 (b). In this diagram, a mixture having a composition in any area designated as I will represent a single phase region. On the other hand, areas marked 2 and 3 represent two-phase region and three-phase region respectively.

According to phase rule, when the three phases are in equilibrium at constant temperature and pressure, the degree of freedom is zero. This means that the compositions of the three layers must be fixed and independent of the overall composition in the area marked 3. Points X, Y and Z represent constant compositions for the three liquid layers in equilibrium.

Examples. System such as succinic nitrile-water-ether exhibits the behaviour corresponding to Fig. 11.20 (a) at higher temperature while at lower temperature, exhibits the behaviour corresponding to Fig. 11.20 (b).

Systems Composed of Two Solids and a Liquid

Systems composed of two solids and a liquid may belong to any one of the following five categories depending on the behaviour of the solid phases:

Type I. Crystallization of pure components only.

Type II. Formation of binary compounds.

Type III. Formation of ternary compounds.

Type IV. Formation of complete series of solid solutions.

Type V. Partial miscibility of solid phases.

In all these types, water will be taken as the liquid because water has by far been regarded the most important crystallization medium.

Type I. Crystallization of pure components only. The isothermal equilibrium diagram for a system composed of water and two solid components *B* and *C* and where the crystallization of pure components occurs is shown in Fig. 11.21.

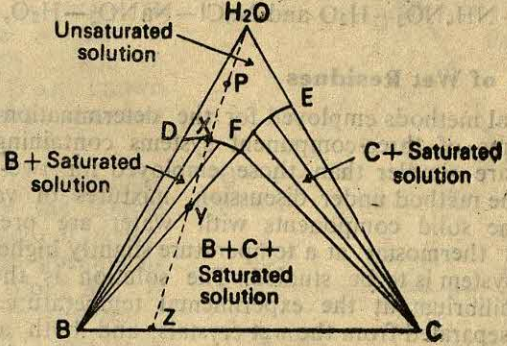


Fig.11.21. Two salts and water system in which the crystallization of pure components occur.

In this diagram, point *D* represents the saturated solution of *B* in water in the absence of *C*. Points between *B* and *D* represent various amounts of solid *B* in equilibrium with saturated solution *D*. Points between *D* and H_2O represent the unsaturated solution of *B*. Similarly point *E* represents the saturated solution of *C* in water in the absence of *B*. Points between *C* and *E* represent various amounts of solid *C* in equilibrium with the saturated solution *E* and points between *E* and H_2O represent the unsaturated solution of *C*. When *C* is added to the solution saturated with *B*, the solubility of the latter changes along the line *DF*. Similarly, addition of *B* to the solution saturated with *C* changes the solubility of the latter along the line *EF*. The line *DF* is, therefore, the saturation solubility curve of *B* in water containing *C*, while *EF* is the corresponding solubility curve of *C* in water containing *B*. At *F*, the point where the two solubility curves intersect, the solution becomes saturated with respect to both *B* and *C*. At this point, since three phases are in equilibrium, the degree of freedom is zero. Hence *F* is called the *isothermal invariant point*. The tie-lines in the diagram connect the concentrations of the saturated solutions with the solid phase in equilibrium with them.

The manner in which such a diagram is used for crystallization is illustrated as follows:

On evaporating isothermally an unsaturated solution represented by *P*, the system moves along the line *PXYZ* which is drawn through apex H_2O and the point *P*. At *X*, *B* begins to crystallize and the composition of the solution changes along the line *XF*. At point *Y*, the composition of the solution is *F* and *C* also begins to crystallize. If the process of evaporation is continued, both *B* and *C* keep on depositing until the point *Z* is reached where the solution disappears completely.

This type of behaviour is exhibited by the systems containing two salts with a common ion and water such as $NH_4Cl-(NH_4)_2SO_4-H_2O$, $NH_4Cl-NH_4NO_3-H_2O$ and $NaCl-NaNO_3-H_2O$, etc.

The Method of Wet Residues

Experimental methods employed for the determination of equilibrium diagrams of three-component systems containing solid and liquid phases are simpler than those employed for two-component systems. In the method under discussion, mixtures of various proportions of the solid components with water are prepared and agitated in a thermostat at a temperature slightly higher than that at which the system is to be studied. The solution is then allowed to attain equilibrium at the experimental temperature. The liquid phase is then separated from the wet crystals, and both are weighed and analyzed for two of the components. In this way, the compositions for saturated solution and the wet residue are obtained. The results for a number of solutions are then plotted on a triangular diagram in the usual manner.

Figure 11.22 shows a series of points obtained in this manner. In the diagram, S_1, S_2, etc., represent compositions of the saturated solutions while R_1, R_2 etc., represent compositions of the corresponding wet residues. In order to ascertain the nature of the solid phases in equilibrium with the various solutions and present in the residue, we employ a graphical scheme known as the *Schreinemakers method of wet residues*. According to this scheme, various tie lines drawn through any corresponding pair of *R* and *S* points must intersect, on extension past *R*, at a common point which is the composition of the solid present. It follows from this reasoning that in this system, *B* is the solid phase for all solutions

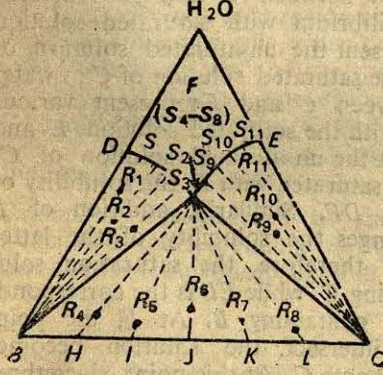


Fig. 11.22. The method of wet residue.

between *D* and *F* and *C* is the solid phase for those between *F* and *E*. Some tie lines drawn in such a manner cut the side *BC* at various points *H*, *I*, *J*, *K* and *L*. This means that the saturated solution represented by *F* is in equilibrium with various proportions of *B* and *C*.

Type II. Formation of binary compounds. When the two salts react to form a compound, a double salt of the general formula *BxCy*, the equilibrium diagram is:

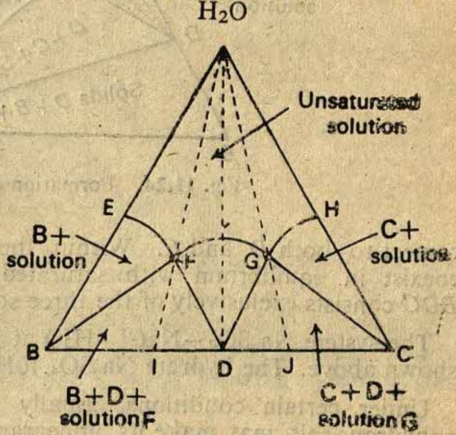


Fig. 11.23. Formation of double salt.

In this diagram, point *D* represents the composition of the salt and line *FG* represents the compositions of solutions saturated with this compound. At point *F*, the solution is saturated with *B* and *D*, while at point *G*, the solution is saturated with *C* and *D*. Points *F* and *G* are known as isothermal invariant points.

In order to determine the stability of the double salt in presence of water, we locate the position of the point *D* along *BC*. If point *D* lies in between *I* and *J*, the salt is said to be congruently saturating as it is possible to prepare saturated solution of salt by adding water to it. This is indicated by the line drawn through the apex H_2O and joining point *D*. On the other hand, if the point *D* lies either on the left of *I* or right of *J*, the salt formed is said to be incongruently saturating as in this case it will not be possible to prepare a saturated solution of the salt by adding water to it, see Fig. 11.23.

The system NH_4NO_3—$AgNO_3$—H_2O shows the formation of the congruently saturating double salt $NH_4NO_3.AgNO_3$ at 30°C while the system KNO_3—$AgNO_3$—H_2O forms incongruently saturating double salt $KNO_3.AgNO_3$ at the same temperature.

If one of the salts, say *B*, forms a hydrate, then the system will have the appearance of phase diagram shown in Fig. 11.24.

In this diagram, point *D* represents the composition of the hydrate formed by *B*, point *E* represents the solubility of hydrate in pure water at the given temperature, while line *EF* represents the solubility of the hydrate in solutions containing *C*. Similarly, line *GF* represents the solubility of *C* in solutions containing hydrate. Within area *DEF*, the hydrate *D* exists in equilibrium with saturated solutions given by the line *EF* while the area *CFG* contains *C* in equilibrium with saturated solutions along the line *GF*. At *F*, the isothermal invariant point, the solution becomes saturated with

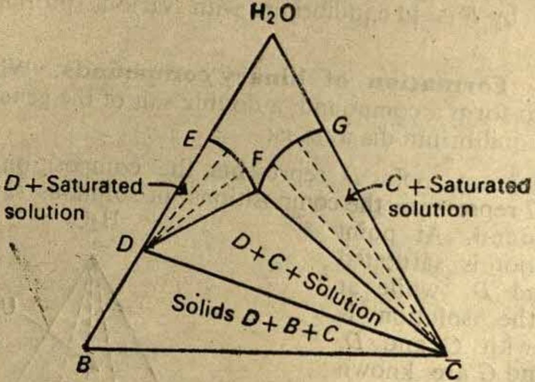


Fig. 11.24. Formation of a hydrate.

respect to both *D* and *C*. Within the area *DFC*, solids *D* and *C* coexist in equilibrium with saturated solution whereas the area *BDC* consists exclusively of the three solids *D*, *B* and *C*.

The system $Na_2SO_4-NaCl-H_2O$ at 15°C gives the phase diagram shown above. The hydrate $Na_2SO_4.10H_2O$ is formed.

Under certain conditions, usually at a higher temperature, the anhydrous salt may make its appearance along with the hydrate of the salt. The phase diagram, then, will have the appearance of Fig. 11.25.

In this diagram, *EF* is the saturation curve for the hydrate, *FG* for the anhydrous salt *B* and *GH* for *C*. *F* and *G* represent two invarient points. The various components present in any region are indicated in the diagram.

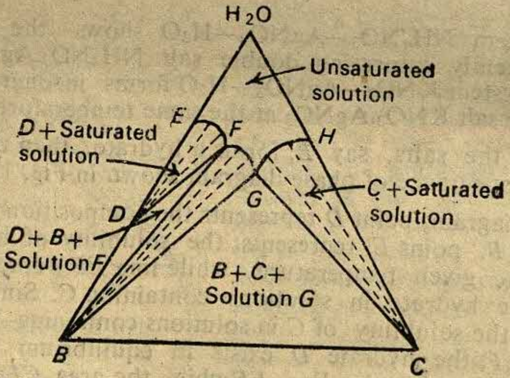


Fig. 11.25. Formation of hydrate and pure components.

The system Na_2SO_4—$NaCl$—H_2O at 25°C exhibits this type of behaviour in which both $Na_2SO_4.10H_2O$ and Na_2SO_4 appear as saturating phases.

A system in which both solid components form a hydrate, will have the phase diagram shown in Fig. 11.26.

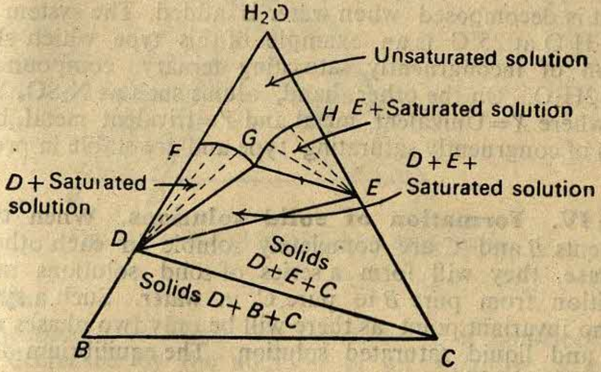


Fig. 11.26. Formation of two hydrates.

Here, points *D* and *E* represent the compositions of the hydrates formed by *B* and *C* respectively. *G* is the isothermal invariant point. Within area *CDE*, solids *D*, *E* and *C* exist together while in the area *BDC*, solids *D*, *B* and *C* exist together.

$MgCl_2$—$CaCl_2$—H_2O at 0°C is an example of such type of system in which the hydrates $MgCl_2.6H_2O$ and $CaCl_2.6H_2O$ are formed.

Type III. Formation of ternary compounds. In some cases, ternary compounds involving all the three components are formed. The equilibrium diagram for such a system is shown in Fig. 11.27.

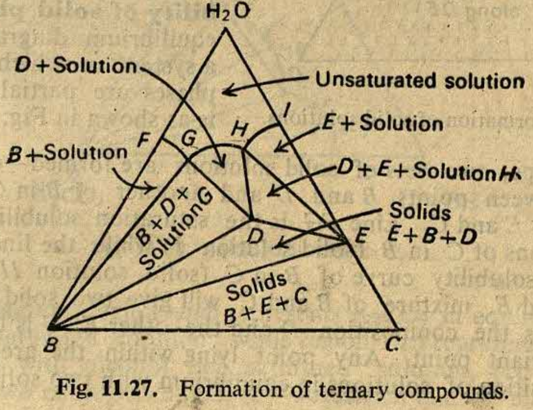


Fig. 11.27. Formation of ternary compounds.

In this diagram, point *E* represents the composition of binary compound (hydrate of *C*) and point *D* represents the composition of ternary compound formed by *B*, *E* and water. *G* and *H* are two isothermal invarient points. Various phases present in different regions are indicated in the diagrams.

In this type, the ternary compound is of incongruently saturating type as it is decomposed when water is added. The system $CaCl_2-MgCl_2-H_2O$ at 25°C is an example of this type which shows the formation of incongruently saturating ternary compound $CaCl_2.MgCl_2,12H_2O$. On the other hand, alums such as $X_2SO_4.Y_2(SO_4)_3.24H_2O$ where *X*=Univalent metal and *Y*=trivalent metal, belong to the class of congruently saturating type and are stable in presence of water.

Type IV. Formation of solid solutions. When two solid components *B* and *C* are completely soluble in each other in the solid phase, they will form a series of solid solutions ranging in composition from pure *B* to pure *C* in water. Such a system will exhibit no invariant point as there will be only two phases *viz.*, solid solution and liquid saturated solution. The equilibrium diagram is shown in Fig. 11.28.

In this diagram, line *DE* represents the compositions of saturated solutions in equilibrium with solid solutions of *B* and *C* of compositions given by the tie lines. In the area above *DE*, only unsaturated solutions can exist. Below *DE*, there are two phases—solid solutions in equilibrium with saturated solutions along *DE*.

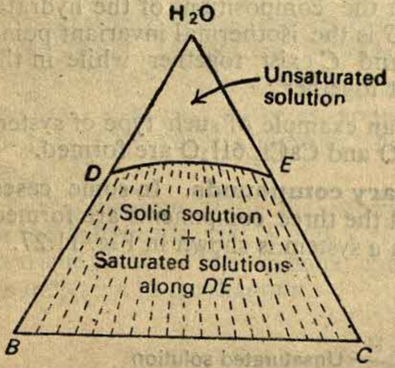


Fig. 11.28. Formation of solid solutions.

Type V. Partial miscibility of solid phases. The equilibrium diagram for such a system in which two solid phases are partially miscible is as shown in Fig. 11.29.

In this type, two sets of solid solutions are formed—one of *C* in *B* lying between points *B* and *D* and another of *B* in *C* lying between points *E* and *C*. Line *FG* is the saturation solubility curve of solid solutions of *C* in *B* (solid solution *I*) while the line *GH* is the saturation solubility curve of *B* in *C* (solid solution *II*). Between points *D* and *E*, mixture of *B* and *C* will give two solid phases one of which has the composition *D* and the other *E*. *G* is the isothermal non-variant point. Any point lying within the area *GDE* will give composition of solutions in equilibrium with two solid solutions *D* and *E*.

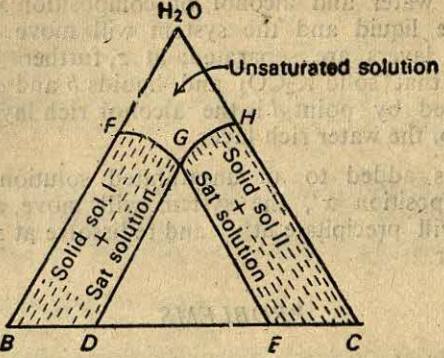


Fig. 11.29. Partial miscibility of solid phases.

Salting Out

The phenomena in which the solubility of a non-electrolyte in water is decreased by the addition of an electrolyte is known as *salting-out*. Thus if some salt is added to a system comprising completely miscible pair of organic liquid and water, two layers are separated—one rich in the organic liquid, the other rich in water. Consider the ternary diagram for $K_2CO_3-H_2O-CH_3OH$ which is typical of the system salt—water—alcohol. See Fig. 11.30.

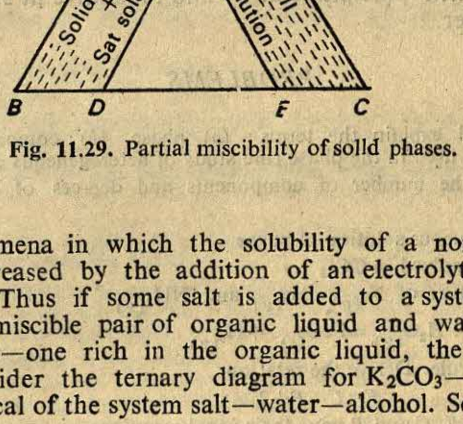


Fig. 11.30. Salting out effect.

In this diagram, region *Bab* represents K_2CO_3 in equilibrium with water-rich saturated solution; while region *Bed* represents K_2CO_3 in equilibrium with alcohol rich saturated solution, *bcd* represents region of two conjugate liquids (*b*—water rich and *d*—alcohol rich) joined by tie line and region *Bbd* represents K_2CO_3 in equilibrium with conjugate liquids *b* and *d*. Suppose that solid K_2CO_3 is added to a mixture of water and alcohol of composition x. Salt will be dissolved in the liquid and the system will move along the line $xyzB$. At y, two layers are separated; at z, further dissolution of K_2CO_3 stops so that solid K_2CO_3 and liquids b and d coexist. The liquid represented by point d is the alcohol rich layer and can be separated from b, the water rich layer.

When water is added to an unsaturated solution of K_2CO_3 in alcohol of composition x', the system will move along the line $x'y'z'$. K_2CO_3 will precipitate at y' and redissolve at z' with further addition of water.

PROBLEMS

1. (*a*) State and explain the terms: (*a*) phase, (*b*) components, and (*c*) degree of freedom, used in the phase rule study of heterogeneous equilibrium.

(*b*) Determine the number of components and degrees of freedom in the following systems:

(*i*) An aqueous solution of sugar

(*ii*) Br_2 dissolved in CCl_4

(*iii*) A mixture of $N_{2(g)}$, $H_{2(g)}$ and $NH_{3(g)}$

(*iv*) $Fe_{(s)} + H_2O_{(g)} = FeO_{(s)} + H_{2(g)}$

2. State phase rule. Derive the relation

$$F = C - P + 2$$

where the symbols F, C and P have their usual meanings.

3. Discuss the application of phase rule to the equilibrium of different phases of water. Label neatly the various portions in the phase diagram. What is triple point?

4. Discuss the application of phase rule to the equilibria met in the case of sulphur system.

5. Discuss and apply the phase rule to the two component system consisting of KI and water.

6. Draw a neat diagram for ferric chloride-water system. How many hydrates of ferric chloride are possible from the study of its phase diagram and of what help is the phase rule in the study of this system?

7. What do you understand by the reduced phase rule equation? Discuss the use of phase rule to the extraction of Ag from lead.

8. Explain the following terms used in the phase rule study of heterogeneous equilibria:

(*a*) Transition point, (*b*) Congruent melting point, (*c*) Eutectic point, (*d*) Invariant system.

9. Write notes on the following:

(*a*) NaCl—water system

(*b*) Sodium sulphate—water system

(*c*) Metastable equilibrium.

10. Explain briefly the application of phase rule to the study of a three-component system.

11. Thermal analysis of the system $A-B$ showed the presence of a line of three-phase equilibrium at 1,000°C and one at 600°. In no case, however, was there more than one half for any cooling curve. A and B melt at 800°C and 1,300°C, respectively and the compound A_2B is known with the melting point

of 700°C. Sketch the simplest phase diagram that conforms with the above data and label all the phase regions.

12. Construct and label the phase diagram from the given thermal data, for binary thallium—gold metal system. At the beginning of each cooling experiment, the binary mixture was homogeneous liquid.

W/W% gold	0	10	20	30	40	60	80	90	100
Cooling Characteristics Temp. °C	302ca	272pa	204pa	200pa	400pa	686pa	910pa	998	1063
		128ca	128ca	128ca	128ca	128ca	127ca	128	ca

13. (*a*) Construct the phase diagram for zinc and magnesium system using the following data:

- (*i*) Melting point of Mg: 665°C
- (*ii*) Melting point of Zn: 500°C
- (*iii*) One eutectic point at 350°C with 20 mole % of Zn and another at 430°C with 92 mole % of Zn.
- (*iv*) A solid compound $MgZn_2$ is formed which melts at 540°C. The maximum is not very sharp. Comment on the stability of the compound.

(*b*) Describe what happens when a mixture of 40 mole % Zn in 60 mole % Mg is cooled from 650°C to 200°C.

14. Construct isothermal equilibrium diagram for a ternary system composed of water and two salts with a common ion. (The two salts do not form a compound). Explain how this diagram is used for crystallization.

15. For the system KNO_3—$NaNO_3$—H_2O, a ternary point exists at 5°C at which the two anhydrous salts are in equilibrium with a saturated solution containing 9.04 per cent by weight of KNO_3 and 41.01 per cent $NaNO_3$. Determine analytically the maximum weight of KNO_3 which could be recovered pure from a salt mixture containing 70 gm of KNO_3 and 30 gm of $NaNO_3$ by crystallization from an aqueous solution at 5°C. Ans. 90.5%

16. Using Fig. 11.29, describe what changes will be observed when:

- (*i*) Water is added to a system containing 50 per cent K_2CO_3 and 50 per cent CH_3OH.
- (*ii*) Methanol is added to a system containing 90 per cent water and 10 per cent K_2CO_3.

Chapter 12

SOLUTIONS

12.1. INTRODUCTION

A solution is defined as a mixture of two or more chemically non-reacting substances whose relative amounts can vary within certain limits. The mixture can be homogeneous or heterogeneous depending upon the size of the particles of the various substances. In homogeneous mixtures, the particles which are of the molecular size ($1m\mu-5m\mu$) [$m\mu$—millimicron], cannot be separated from each other by mechanical means and the composition is uniform all throughout. Such a homogeneous mixture is called a *true solution* *e.g.*, solution of sugar or salt in water. In heterogeneous mixtures, the particles are present as larger aggregates (size greater than 200 $m\mu$). These particles are readily discernible and can be separated from each other by simple mechanical methods. Such a heterogeneous mixture is called a *coarse mixture e.g.*, mixture of salt and sugar.

There are certain other types of mixtures which appear homogeneous to the naked eye but, when seen through an ultramicroscope, are found to be heterogeneous. Such types of mixtures are called *colloidal solutions e g.*, milk. In colloidal solutions, the particles are of intermediate size ($5\ m\mu-200\ m\mu$).

The definition of a solution as given above is not restricted to either the state of aggregation or the relative amounts of the constituents. Hence a solution may be gaseous, liquid or solid of variable composition within wide limits. This latter fact excludes pure compounds from the classification of solution because a fixed and definite ratio exists among the constituents in a compound.

The components of a solution are frequently referred to as *solute* and *solvent*. A solute is generally taken as the substance which dissolves and a solvent is a substance in which solution takes place. Thus for solutions in which one component is a gas or a solid and the other is a liquid, the former is the solute and the latter is the solvent. When both the components are liquid present together in different proportions, the major component is considered the solvent and the minor component the solute. However, for solutions where the two liquid components of a solution are present in equal proportions, one is justified to call each as either the solvent or solute.

12.2. TYPES OF SOLUTIONS

Although solutions containing many components are encountered in chemistry, we shall confine ourselves to binary solutions *i.e.*, solutions containing two components. Since the components can be gaseous, liquid or solid, it is possible to have binary solutions belonging to any one of the classes given below in Table 12.1.

TABLE 12.1

Examples of possible types of binary solutions

S. No.	*Solute*	*Solvent*	*Examples*
1	Gas	Gas	Any mixture of gases, air (Partial and total pressures governed by Dalton's law).
2.	Gas	Liquid	Ammonia in water, aerated water.
3.	Gas	Solid	Hydrogen in Palladium.
4.	Liquid	Gas	Vaporisation of a liquid into a gas.
5.	Liquid	Liquid	Water in alcohol.
6.	Liquid	Solid	Liquid benzene in solid iodine.
7.	Solid	Gas	Sublimation of a solid into a gas.
8.	Solid	Liquid	Sugar in water.
9.	Solid	Solid	Lead in silver, copper in nickel etc.

Of all these types, we shall limit ourselves to the study of solutions belonging to types 2, 5 and 8 only in this chapter.

12.3. MODES OF EXPRESSING COMPOSITION (CONCENTRATION) OF SOLUTIONS

The composition *i.e.*, the relative amounts of each component in a solution, can be expressed in a number of quantitative ways. Consider a binary solution of two components A and B. The component B is the solute and the component A is the solvent. The notations adopted are given below:

W_A, W_B=Weight (mass) in grams of A and B

n_A, n_B=Number of moles of A and B

V_A, V_B=Volume in litres of A and B

V=Total volume of the solution in litres.

The various terms which are commonly used for expressing the composition of the solutions are the following:

(1) *Weight per cent*. The weight per cent of component B in the solution is given by,

$$\text{weight per cent of } B = \frac{W_B}{W_A + W_B} \times 1C0$$

This is the simplest and the most useful concentration unit.

(2) *Weight ratio*. This is given by $\frac{W_B}{W_A}$. Generally solubilities are often expressed in terms of this unit.

(3) *Volume per cent*. Volume per cent of B in A is given by:

$$\text{Volume per cent of } B = \frac{V_B}{V} \times 100$$

This is limited to liquid-liquid solutions.

(4) *Molarity* (M). This is given by the number of moles of the solute per litre of the solution. The molarity of B in the solution is given by

$$M_B = \frac{n_B}{V}$$

(5) *Formality*. In some cases, this term is used for solutions of ionic substances. Formality of a solution is given by the formula weight of the solute dissolved in one litre of the solution.

(6) *Normality* (N). Normality of a solution is given by the number of equivalents of the solute dissolved in one litre of solution.

(7) *Molality* (m). This is given by the number of moles of solute per 1000 grams of the solvent. Molality of A in the solution is given by

$$m_B = \frac{n_B}{W_A} \times 1000$$

4th, 6th and 7th types are most useful for dilute solutions.

(8) *Mole fraction* (X). Mole fraction of any component in a solution is given by the number of moles of that component divided by the total number of moles of all the components in the solution. Mole fraction of B in the solution is given by

$$X_B = \frac{n_B}{n_A + n_B}$$

The sum of all the mole fractions of a solution is always equal to unity. In the present case, we have two components:

$$X_A + X_B = 1$$

If instead of the number of moles, weights of the constituents and their molecular weights are given, the mole fraction is given by

$$X_B = \frac{W_B/M_B}{W_A/M_A + W_B/M_B}$$

where M_A and M_B are the molecular weights of the components A and B respectively.

Of all these methods, those which are expressed on volume basis such as 3rd, 4th, 5th and 6th, will change with temperature because of the thermal expansion or contraction of the solution. Other methods, which are expressed on a weight basis, will be independent of temperature and the concentration will remain same at all the temperature.

Problem 12.1. Calculate the weight per cent of each component of a solution which contains 40.10 grams of sodium chloride, 20.20 grams of methyl alcohol and 100.20 grams of water. Also calculate the molarity of sodium chloride and methyl alcohol for the solution assuming that the density of the solution is 1.10 gms/ml. (Molecular weights of NaCl and CH_3OH are 58.5 and 32.0 respectively.)

Solution. Weight per cent of NaCl

$$=\frac{40.1}{40.1+20.2+100.2}\times 100=25.0\%$$

Weight per cent of CH_3OH

$$=\frac{20.2}{40.1+20.2+100.2}\times 100=12.5\%$$

Since the total percentage is 100. The weight per cent of water

$$=100-(25.0+12.5)=62.5\%$$

Alternatively, weight per cent of water

$$=\frac{100.2}{40.1+20.2+100.2}\times 100=62.5\%$$

Calculation of Molarity

For NaCl, $n_{\text{NaCl}}=\dfrac{40.1}{58.5}$

Therefore, $$M_{\text{NaCl}}=\frac{40.1/58.5}{(40.1+20.2+100.1)\text{ gm solution}}\times\frac{1000}{\frac{1\text{ gm of solution}}{1.10\text{ gm of solution}}}$$

$$=4.70\ M$$

Similarly, for CH_3OH,

$$\because\ n_{CH_3OH}=\frac{20.2}{32.0}$$

$$M_{CH_3OH}=\frac{20.2/32.0}{(40.1+20.2+100.2)\text{ gm solution}}\times\frac{1000}{\frac{1\text{ gm of solution}}{1.10\text{ gm of solution}}}$$

$$=4.33\ M$$

Problem 12.2. Determine the molarity of a solution containing 86.53 grams of sodium carbonate (Molecular weight—105.99) per litre of the solution in water at 20°C. The density of the solution at this temperature is 1.0816 gm/ml. Also find the molarity of the solution.

Solution. (*i*) **Calculation of Molarity**

Since the number of mole of Na_2CO_3,

$$n_{Na_2CO_3}=\frac{86.53}{105.99}=0.8164 \text{ mole}$$

Molarity of the solution $=\frac{0.8164}{1 \text{ litre}}=0.8164$ mole/litre

(*ii*) **Calculation of Molality**

Since the density of solution is 1.0816 gm/ml, the mass of 1 litre of the solution is

$$=1.0816\times1000=1081.6 \text{ gm/litre.}$$

Now this quantity of solution contains 86.53 gm Na_2CO_3

Weight of water $=1081.6-86.53=995.1$ gm

Molality of the solution $=\frac{0.8164\times1000}{995.1}$

$=0.8203$ m.

12.4. SOLUTION OF GASES IN LIQUIDS

Most of the gases are easily soluble in liquids and form true solutions. Thus oxygen of air is dissolved by water of rivers and seas and this is responsible for the respiration of fish and other aquatic animals. The solution of a gas in a liquid is an example of a two-component system. The two components are gas and the liquid ($C=2$). Since there are two phases *i.e.*, $P=2$ (gas and solution), according to the Phase Rule,

$$F+P=C+2$$
$$F+2=2+2$$
or
$$F=2$$

Thus the system is bivariant. If the temperature is kept constant, both pressure of gas and composition of solution, *i.e.*, the solubility of the gas, can vary. If the composition is maintained constant, pressure and temperature are variable.

It is clear that the solubility of a gas in a liquid depends on the temperature and pressure. Various other factors on which solubility is also dependent are the nature of the gas and the nature of the liquid solvent.

At a given temperature and pressure, the solubility of different gases in the common solvent varies. Those gases which undergo chemical interaction with water *e.g.*, ammonia, carbon dioxide, sulphur dioxide, hydrogen chloride, etc., are the most soluble in water.

$NH_3+H_2O\rightleftharpoons NH_4OH$ (Ammonium hydroxide)
$CO_2+H_2O\rightleftharpoons H_2CO_3$ (Carbonic acid)
$SO_2+H_2O\rightleftharpoons H_2SO_3$ (Sulfurous acid)
$HCl+H_2O\rightleftharpoons H_3O^++Cl^-$

For other gases, solubility depends on the ease of liquefaction. Thus those gases which can be easily liquefied *e.g.*, carbon dioxide, sulphur dioxide etc., are fairly soluble in the common solvents. On the other hand, the gases which cannot be easily liquefied such as permanent gases *e.g.*, oxygen, nitrogen, hydrogen, helium etc., are least soluble in water.

Since the solubility of a gas in a liquid is generally determined by measuring the volume; rather than the weight that dissolves, it is frequently expressed in terms of absorption coefficient, α, introduced by R. Bunsen (1857). This is defined as the volume of gas, reduced to 0°C and 1 atmosphere pressure, dissolved by unit volume of the solvent at the experimental temperature under a partial pressure of 1 atmosphere of the gas.

The absorption coefficients of some of the common gases at 20°C in three different common solvents are given in Table 12.2.

TABLE 12.2

Bunsen absorption coefficients of gases at 20°C

Solvent	*Hydrogen*	*Helium*	*Nitrogen*	*Oxygen*	*Carbon dioxide*
Water	0.017	0.009	0.015	0.028	0.025
Ethanol	0.080	0.028	0.130	0.143	0.177
Benzene	0.066	0.018	0.104	0.163	0.153

The solubility of the gas can be expressed in moles per litre at the temperature of the experiment and under a pressure of 1 atmosphere if the absorption coefficient is divided by 22.4 (volume in litres occupied by 1 mole of the gas at 0°C and 1 atmosphere pressure).

Effect of temperature on solubility. It has been observed in most of the gases that when they dissolve in liquid, usually heat is given out (Exception: solubility of H_2, O_2 and the inert gases in certain organic liquids). Hence in accordance with Le-Chatelier principle, solubility of a gas in a liquid will decrease with rise of temperature. Thus it is possible to remove the dissolved gas from solution just by boiling it. However, in case of conc. HCl, it is not possible because by boiling it, the whole of HCl, just like a definite compound, will evaporate off unchanged in composition at a particular temperature.

Effect of pressure on solubility—Henry's Law. The effect of pressure on the solubility of a gas in a particular liquid at some constant temperature can be readily understood in terms of Henry's Law which states that:

"At constant temperature, the mass of a gas dissolved in a unit volume of a liquid is directly proportional to the pressure of the gas above the liquid at equilibrium."

Mathematically, $m \propto p$

or $$m = kp \qquad \ldots (12.1)$$

where m is the mass of the gas dissolved by unit volume of solvent, p is the pressure of the gas in equilibrium with the solution and k is a proportionality constant known as Henry's Law constant. The magnitude of k depends on the nature of the gas and liquid, temperature and the units in which pressure is expressed.

From equation (12.1), it is evident that for the validity of Henry's Law, the plot of the solubility of the gas against the equilibrium pressure at a constant temperature should be a straight line passing through the origin as shown in Fig. 12.1.

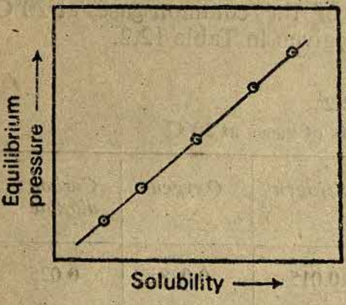


Fig. 12.1. Variation of solubility of a gas with pressure.

It has been observed that for the strict applicability of Henry's Law—(*i*) temperature should be high (*ii*) pressure should be low and (*iii*) no chemical reaction should take place between the dissolved gas and the solvent (such as compound formation between the dissolved gas and solvent, association of the gas into more complex molecules or dissociation of the gas).

Thus for the solubility of HCl and NH_3 in water, Henry's Law altogether fails if the total solubility is considered. This is due to the involvement of the following reactions:

$$HCl\ (gas) = HCl\ (dissolved)$$

$$HCl\ (dissolved) + H_2O = H_3O^+ + Cl^-$$

and $$NH_3\ (gas) = NH_3\ (dissolved)$$

$$NH_3\ (dissolved) + H_2O = NH_4OH$$

$$NH_4OH = NH_4^+ + OH^-$$

In such cases where the dissolved gas reacts with the solvent, Henry's Law is applicable only to the amount of the gas which is in the free or uncombined state in the solution and will fail if the total solubility is considered.

When a mixture of several gases is dissolved simultaneously, Henry's Law is found to be still applicable to each gas independent of the pressure of the other gases present in the mixture. It is, therefore, possible to say that the solubility of each gas from a mixture of gases is proportional to its own partial pressure in the mixture. The proportionality constant k, will of course be not same for different gases.

12.5. HENRY'S LAW AND RAOULT'S LAW

According to Henry's Law, $m=kp$, where m is the mass of the gas dissolved in unit volume of solvent and p is the equilibrium pressure. If m is replaced by $\frac{W_2}{W_1}$ where W_2 is the weight of the gas dissolved in W_1 gms of the solvent, Henry's Law relationship becomes

$$\frac{W_2}{W_1}=k'p_2 \qquad \ldots (12.2)$$

where p_2 is the pressure of the gas.

Dividing the two masses by their respective molecular weights, we get

$$\frac{W_2/M_2}{W_1/M_1}=k'p_2 \qquad \ldots (12.3)$$

or

$$\frac{n_2}{n_1}=k'p_2 \qquad \ldots (12.4)$$

where $n_2\left(=\frac{W_2}{M_2}\right)$ and $n_1\left(=\frac{W_1}{M_1}\right)$ are the number of moles of solvent and solute respectively. If the gas dissolved has very little solubility, solution will be dilute so that

$$\frac{n_2}{n_1}\approx\frac{n_2}{n_1+n_2}$$

$$\therefore \qquad \frac{n_2}{n_1+n_2}=X_2=k''p_2 \qquad \ldots (12.5)$$

where X_2 is the mole fraction of the gaseous solute in the saturated solution. Equation (12.5) suggests that the solubility of a sparingly soluble gas, expressed in mole fraction, is also proportional to the pressure of the gas.

Alternatively, it also suggests that p_2, which may be taken as the vapor pressure of a volatile solute, is proportional to the mole fraction of the solute in the solution. Hence Henry's Law can also be stated as follows:

In a dilute solution, the vapor pressure of a solute is directly proportional to its mole fraction. In cases where the law is applicable over the whole range of concentration—from an infinitely dilute solution *i.e.*, pure solvent to the pure (liquid) solute, p_2 will become the vapor pressure of the pure solute ($=p_2^\circ$) when X_2 is unity.

Hence

$$1=k''p_2^\circ$$

or

$$k''=\frac{1}{p_2^\circ} \qquad \ldots (12.6)$$

Substituting this value of k'' into equation (12.5), we get

$$X_2 = \frac{p_2}{p_2^\circ}$$

or
$$p_2 = X_2 p_2^\circ \qquad \ldots (12.7)$$

Equation (12.7) is an equation of Raoult's Law for a volatile solute.

This shows that Raoult's can be regarded as a special case of Henry's Law and all systems obeying Raoult' Law must agree with Henry's Law. The reverse of this is also true provided Henry's Law is applicable over the whole range of concentration.

12.6. MIXTURES OF TWO LIQUIDS

The two liquids which do not react chemically when brought together gives rise to three possibilities as regards their mutual solubility—the two liquids may be completely miscible, completely immiscible or partially miscible. Thus, the following three pairs of liquids are possible.

(*i*) Liquid pairs which dissolve in each other in all proportions and have no saturation limit. Such liquid pairs are said to be *completely miscible e.g.*, water-ethyl alcohol; benzene-toluene; water-acetic acid; water-glycerol, etc.

(*ii*) Liquid pairs which do not dissolve at all in each other. Such liquid pairs are said to be *completely immiscible e.g.*, water-mercury.

(*iii*) Liquid pairs which dissolve in each other only to certain limits. Such liquid pairs are said to be *partially miscible e.g.*, water-ether, water-phenol etc.

Generally it has been observed that those liquids which have similar chemical structure are completely miscible while liquids which have different chemical structures are completely immiscible. Thus water is completely miscible with alcohol because the two are chemically similar. But since mercury is very different chemically from water, the two are completely immiscible. Similarly, benzene dissolves hydrocarbons.

12.7. THE IDEAL SOLUTION AND RAOULT'S LAW

Just as the concept of an ideal gas as a criterion of gas behaviour has been very helpful in predicting thermodynamics and other properties of gases and vapors, so too, it will also be very helpful to set up a similar concept in the case of solution. The concept of an ideal solution will act as a guide in discussing the theory of solutions on the basis of certain simple laws. For practical purposes, an ideal solution may be defined as a solution in which there is complete uniformity of cohesive forces *i.e.*, the molecules in an ideal solution will exert the same force on each other irrespective of their nature. Thus if we have an ideal solution of two components, A and B, the intermolecular forces between A and A, B and B, and A and B, will be same. Other characteristic properties of an ideal solution are—no heat is given out or absorbed in the formation of solution and total volume is equal to the sum of volume of individual components.

If the two components of a solution are volatile, they will have a natural tendency of escaping into vapor phase and exert a definite vapor pressure. When the solution is an equilibrium with vapor, the total pressure above the solution will be equal to the sum of the partial vapor pressures of the individual components in accordance with Dalton's Law of partial pressures, If P_A and P_B are the partial vapor pressures of two volatile and miscible components A and B, the total pressure, P, is P_A+P_B. The assumption made here is that vapors behave as ideal gases. The partial vapor pressure of each component of an "*ideal solution*" can be easily determined from Raoult's Law. This law states that the *partial vapor pressure of any volatile constituent of a solution is equal to the vapor pressure of the pure constituent multiplied by the mole fraction of that constituent in solution over the whole concentration range at all temperatures.*

Thus if X_A and X_B are the mole fractions of the two components in the solution and P°_A and P°_B are the vapor pressures of the pure liquids A and B, then from Raoult's Law, the vapor-pressures of the two constituents above the solution are

$$P_A=P^\circ_A X_A \quad \text{.., (12.8)}$$

and

$$P_B=P^\circ_B X_B \quad \text{... (12.9)}$$

Therefore, the total vapor pressure P of the solution is

$$P=P_A+P_B=P^\circ_A X_A+P^\circ_B X_B \quad \text{... (12.10)}$$

Again, since $X_A+X_B=1$

or $X_A=1-X_B$

Equation (12.10) can also be written as

$$P=P^\circ_A(1-X_B)+P^\circ_B X_B$$
$$=(P^\circ_B-P^\circ_A)\ X_B+P_A \quad \text{... (12.11)}$$

Equation (12.11) gives the total vapor pressure above a solution in terms of the vapor pressures of the two pure constituents and the mole fraction of one of the constituents. At a particular temperature, since P_A° and P_B° are constants, a plot of P versus X_B should be a straight line with the slope $(P_B^\circ-P_A^\circ)$ and an intercept P_A° at $X_B=0$ as shown by the solid line in Fig. 12.2.

In Fig. 12.2, the dotted lines represent plots of equations (12.8) and (12.9) for the partial pressures of the two components A and B against their respective mole fractions. Each dotted line is a straight line and passes through the origin indicating that both components are ideal liquids. The solid line gives the total vapor pressure of the mixtures of A and B of all compositions and is obtained by joining P°_A and P°_B. The total pressure at all intermediate concentrations can be obtained by taking the sum of the partial pressures of the two components corresponding to the particular concentration

Thus at $X_B=0.2$,

$$P=P_A+P_B$$

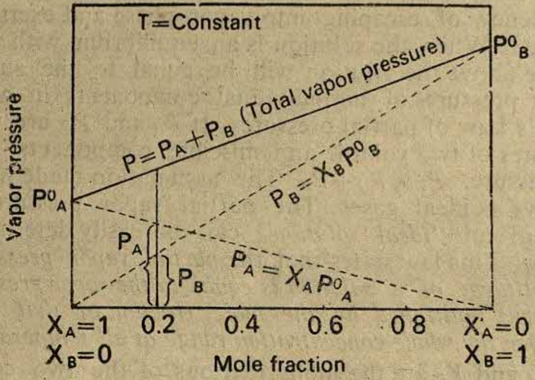


Fig. 12.2. Total and partial vapor pressure curves for an ideal solution over the whole concentration range at constant temperature.

The type of the plot as shown above are obtained only for ideal solutions. Actually, in practice it has been found that a few binary solutions *e.g.*, benzene-toluene; ethylene bromide-ethylene chloride, *n*-hexane-*n*-heptane, carbon tetrachloride-silicon tetrachloride, water-methyl alcohol; *n*-butyle chloride-*n*-butyle bromide, chlorobenzene-bromobenzene systems, obey Raoult's law over the whole concentration range at certain temperatures. The ideality of such solutions are attributed to their chemical similarity. Due to their similarity, the inter-molecular forces in the solution of the two liquids will be uniform.

12.8. NON-IDEAL (REAL) SOLUTIONS OF MISCIBLE LIQUIDS

As pointed out earlier, only a few binary solutions strictly obey Raoult's law over the whole range of concentration. In many cases, mixtures of two miscible liquids form non-ideal solutions over most of the concentration range and the systems exhibit either a positive or negative deviation from Raoult's law. These deviations from Raoult's law are generally observed for systems in which the two components *A* and *B* of the liquid mixture have different molecular structure. Due to differences in the molecular structure, intermolecular forces will not be same. If the attraction between the different molecules *i.e.*, *A* and *B* molecules is weaker than between similar molecules *i.e.*, between *A-A* and *B-B* molecules, the escaping tendency from the solution into the vapor of the molecules of each kind will be more than from the two pure liquids. The partial vapor pressures of *A* and *B* will, therefore, be greater than predicted from Raoult's law. Such a system will exhibit positive deviation from Raoult's law. The shape of the curve is shown in Fig. 12.3.

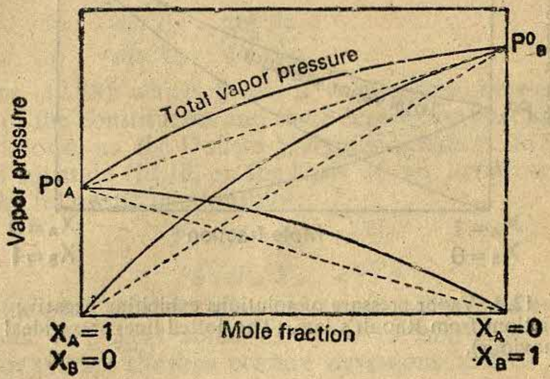


Fig. 12.3. Vapor pressure solutions exhibiting positive deviations from Raoult's law. (The dotted lines show ideal behaviour.)

In this case, the system exhibits a *maximum* in the total vapor pressure curve. Examples of this type of system are: acetone-carbon disulphide; chloroform-ethyl alcohol; benzene-cyclohexane etc.

Large positive deviations are observed in the case of mixtures of two liquids which markedly differ in polarity, internal pressure, length of hydrocarbon chain and degree of association *e.g.*. an alcohol and a hydrocarbon. If the difference in polarity between the two liquids is quite small *e.g.*, ether and acetone; or both the two liquids are non-polar *e.g.*, carbon tetrachloride and heptane, the positive deviation from Raoult's law are small.

If the attraction between different molecules *i.e.*, between *A-B* molecules is stronger then between identical molecules *i.e.*, between *A-A* and *B-B* molecules, the escaping tendency from the solution into the vapor of molecules of each kind will be smaller than the two pure liquids. As a result of this, partial vapor pressure of each constituent will be smaller than that predicted from Raoult's law and the system will exhibit *negative deviation* from Raoult's law. The shape of the curve is shown in Fig. 12.4.

In this case, the system exhibits a minimum in the total vapor pressure curve. The examples of this type of system are pyridine-acetic acid; chloroform-acetone; water-nitric acid, formic acid or halogen acids etc.

The relationship between the mole fractions of the constituents in the mixture and their partial vapor pressure can also be deduced theoretically from Gibbs-Duhem equation as follows:

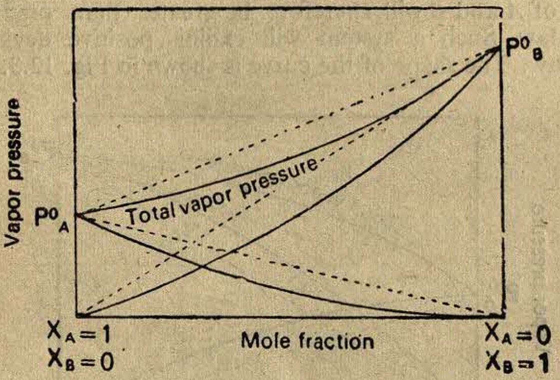


Fig. 12.4. Vapor pressure of solutions exhibiting negative deviations from Raoult's law. (The dotted lines show ideal behaviour).

For a system consisting of two components A and B, Gibbs-Duhem equation can be written as:

$$n_A d\mu_A = -n_B\, d\mu_B \qquad \ldots (12.12)$$

where the terms n and μ represent the number of moles and chemical potential of two respective components in the given mixture.

Dividing both sides of equation (12.12) by $n_A + n_B$, we get

$$X_A d\mu_A = -X_B d\mu_B \qquad \ldots (12.13)$$

where X_A and X_B are their respective mole fractions.

Now, since $X_A + X_B = 1$

$X_B = 1 - X_A$

or $dX_B = -dX_A$

Hence

$$X_A \frac{d\mu_A}{dX_A} = -X_B \frac{d\mu_B}{dX_A} = X_B \frac{d\mu_B}{dX_B} \qquad \ldots (12.14)$$

Again, the chemical potential of any component of a mixture is given by:

$$\mu = \mu^\circ + RT\, ln p \qquad \ldots (12.15)$$

where p is the partial vapor pressure of that component at constant temperature and pressure. Differentiating equation (12.15) with respect to X_A and X_B, we get:

$$\frac{d\mu_A}{dX_A} = \frac{RT\, dln\, P_A}{dX_A} \qquad \ldots (12.16)$$

and $$\frac{d\mu_B}{dX_B}=RT\ \frac{dlnP_B}{dX_B} \qquad \ldots (12.17)$$

Combinations of equations (12.16) and (12.17) with equation (12.14) gives:

$$X_A\frac{dln\ P_A}{dX_A}=X_B\ \frac{dln\ P_B}{dX_B}$$

or $$\frac{dln\ P_A}{dln\ X_A}=\frac{dln\ P_B}{dln\ X_B} \qquad \ldots (12.18)$$

Equation (12.18) which gives a relationship between the mole fractions of the constituents and their respective partial vapor pressures is known as the Duhem-Margules equation. Margules (1895) integrated equation (12.18) on the basis of an arbitrary assumption and got the following relationships:

$$P_A=P_A^\circ\ X_A\ .\ e^{\alpha X^2{}_B}$$

and $$P_B=P_B^\circ X_B\ .\ e^{\alpha X^2{}_A}$$

The value of α which is some constant is same for a both the two components. For ideal solutions, $\alpha=0$; for non-ideal solutions, α is positive for systems showing positive deviations and is negative for those which show negative deviations.

12.9. RELATIONSHIP BETWEEN THE COMPOSITION OF A SOLUTION AND THE COMPOSITION OF THE VAPOR ABOVE IT

As we know, the concentration of any ideal solution is governed by Raoult's law and the concentration of the vapor above the solution is governed by Dalton's law of partial pressure. Thus, for the system as considered under ideal solution, if Y_B is the mole fraction of B in the vapor above a solution of composition X_B, then according to Dalton's Law:

$$P_B=Y_BP$$

or $$Y_B=\frac{P_B}{P} \qquad \ldots (12.19)$$

Substituting the value of P_B from equation (12.9) and of P from equation (12.11), we get:

$$Y_B=\frac{P_B^\circ\ X_B}{(P_B^\circ-P_A^\circ)\ X_B+P_A^\circ} \qquad \ldots (12.20)$$

This equation gives the relationship between the composition of B in the vapor phase and the composition of B in the solution. Equation (12.20) suggests that Y_B and X_B are different and will be same only when $P_B^\circ=P_A^\circ$ *i.e.*, the pure liquids A and B have the same vapor pressure Equation. Eq. (12.20) can also be written as:

$$\frac{\text{Mole fraction of } B \text{ in vapor}}{\text{Mole fraction of } B \text{ in solution}}=\frac{Y_B}{X_B}$$

$$=\frac{1}{X_B+\frac{P_A^\circ}{P_B^\circ}X_A^\circ} \qquad \ldots (12.21)$$

$$\left[\begin{aligned} &\text{Since} \quad Y_B=\frac{P_B}{P} \\ &\qquad\qquad =\frac{P_B^\circ P_B}{P_B^\circ X_E+P_A^\circ X_A}, \\ &\text{or} \quad \frac{Y_B}{X_B}=\frac{P^\circ_B}{P_B^\circ X_B+P_A^\circ X_A} \\ &\qquad\qquad =\frac{1}{X_B+\frac{P_A^\circ}{P_B^\circ}X_A} \end{aligned}\right]$$

It follows from equation (12.21) that if $P_A^\circ < P_B^\circ$ *i.e.*, the component A is less volatile than the component B, the denominator is less than 1 and the ratio Y_B/X_B is greater than 1. This means that the concentration of B will be more in the vapor phase than in the solution. The general conclusion that follows is that for a system obeying Raoult's law, *the vapor is richer in the more volatile component.*

The same result is applicable to non-ideal solutions also. With the help of equation (12.20), it is possible to calculate the composition of the vapor in equilibrium with a solution containing known amounts of the two components. Knowing the composition of the vapor corresponding to any composition in the solution, a vapor pressure—vapor composition curve at any definite temperature can be constructed. Such a plot for an ideal solution is shown in Fig. 12.5.

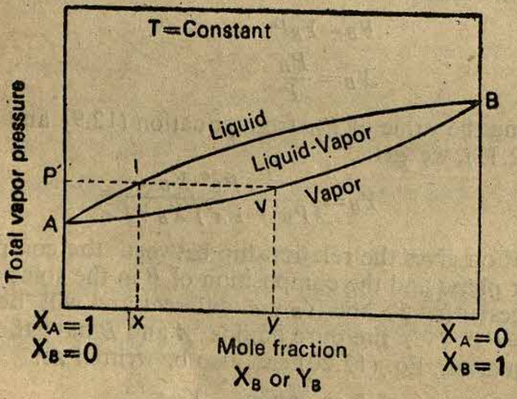


Fig. 12.5. Liquid-vapor equilibria (Temperature is constant).

The curve marked "Liquid" is known as the Liquid composition curve. It gives the total pressure above the solution as a function of mole fraction X_B. The curve marked "Vapor" is known as the vapor composition curve and gives the composition of the vapor in equilibrium with the solution having the total vapor pressure indicated on the ordinate. For example, the composition of vapor corresponding to a solution with composition $X_B = X$ and total pressure P (point l on the liquid composition curve) is $Y_B = V$ (point V on the vapor composition curve). The line lV is known as the *tie line* because it ties together the two phases in equilibrium.

The vapor pressure-liquid composition curves along with the corresponding vapor pressure—vapor composition curves for non-ideal solutions exhibiting positive and negative deviation from Raoult's law are shown in Fig. 12.6 (a) and (b). It should be noted that for each type the vapor composition curve lies below the liquid composition curve indicating that the vapor is richer in the more volatile constituent. Again in the diagrams for non-ideal solutions, the two curves are in contact at the points M and N corresponding to the maximum and minimum vapor pressure respectively. At these points, therefore, liquid and vapor in equilibrium will have the same composition. For convenience, each of the two diagrams for non-ideal solution may be divided into two parts by a vertical line passing through M and N respectively. Each part will have the appearance of the system obeying Raoult's law. Thus these two diagrams can be regarded as being composed of two curves—one for pure A and the solution of maximum or minimum vapor pressure M or N respectively and the other of solution of miximum or minimum vapor pressure M or N and pure B.

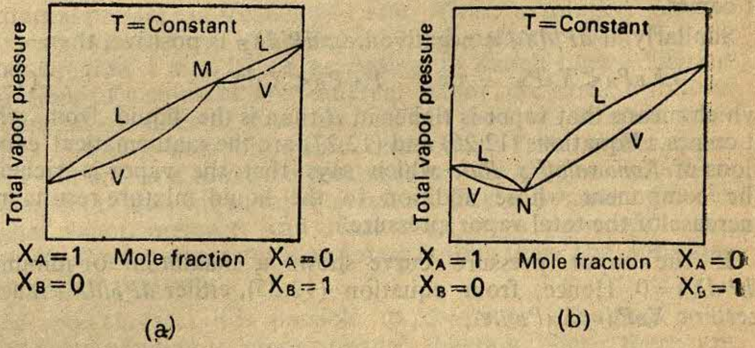


Fig. 12.6. Liquid-vapor equilibria for non-ideal solutions exhibiting positive and negative deviations. (L represents liquid composition curve and V represents vapor composition curve.)

The composition of the vapor in equilibrium with a liquid at a given temperature can be theoretically determined from Duhem-Margules equation as follows:

Duhem-Margules equation for two components *A* and *B* is:

$$\frac{d\ln P_A}{d\ln X_A}=\frac{d\ln P_B}{d\ln X_B} \quad \ldots (12.22)$$

where the terms *X* and *P* represent the mole fraction and partial pressure of the two components under consideration.

This equation can also be written as:

$$\frac{X_A\, dP_A}{P_A\, dX_A}=\frac{X_B\, dP_B}{P_B\, dX_B} \quad \ldots (12.23)$$

Since $X_A+X_B=1$ or $dX_A=-dX_B$

Equation (12.23) can also be written as:

$$\frac{X_A.dP_A}{P_A.dX_A}+\frac{X_B.dP_B}{P_B.dX_A}=0 \quad \ldots (12.24)$$

Again, since the total pressure *P* is given by:

$$P=P_A+P_B$$

Differentiating *P* with respect to X_A, we get:

$$\frac{dP}{dX_A}=\frac{dP_A}{dX_A}+\frac{dP_B}{dX_A}$$

$$=\frac{dP_B}{dX_A}\left(1-\frac{X_B\, P_A}{X_A\, P_B}\right) \quad \ldots (12.25)$$

Now the value of dP_B/dX_A must be negative as it is equal to $-dP_B/dX_B$. Thus it follows that if dP/dX_A is to be positive, $\left(1-\frac{X_BP_A}{X_AP_B}\right)$ must be negative which can be possible if $X_BP_A>X_AP_B$ or $P_A/P_B>X_A/X_B$. ... (12.26)

This means that vapor is richer in *A* than is the liquid from which it comes.

Similarly, if dP/dX_A is negative *i.e.*, dP/dX_B is positive, then

$$X_BP_A<X_AP_B \quad \text{or} \quad P_A/P_B<X_A/X_B \quad \ldots (12.27)$$

which means that vapor is richer in *B* than is the liquid from which it comes. Equations (12.26) and (12.27) are the mathematical expressions of *Konowaloff's Rule* which says that the vapor is richer in the component whose addition to the liquid mixture results in an increase of the total vapor pressure.

If the vapor pressure curve shows a maximum or minimum, $dP/dX_A=0$. Hence, from equation (12.25), either dP_B/dX_A must be zero or $X_BP_A=X_AP_B$ *i.e.*,

$$\frac{X_A}{X_B}=\frac{P_A}{P_B}$$

The former condition is not possible because it would mean that the partial vapor pressure would remain constant in spite of a change of concentration. Hence, for a solution showing maximum or minimum total vapor pressure, the later condition holds *i.e.*

$$\frac{X_A}{X_B}=\frac{P_A}{P_B}$$

which means that *at the point of maximum or minimum in the total vapor pressure curve, the composition of the solution and vapors are identical.*

12.10. BOILING POINT DIAGRAMS OF BINARY MISCIBLE LIQUID MIXTURES

In the three types of diagrams discussed above, the temperature is constant. Since the vapor above any solution is always richer in the more volatile component than the solution, the components of a solution can be easily separated as discussed below.

By removing the vapors above a solution, the solution, can be made richer in the less volatile component. If the vapors are condensed to form a new liquid solution, the vapors above this new solution will again be richer in the more volatile component than the solution from which they came. By repeating several times the process of removing the vapors from the 'newer' solution and condensing them, it is possible to obtain a concentration of more volatile component in the vapor and a concentration of less volatile component in the solution. This process of concentrating the components is called *isothermal fractional distillation* because the process takes place at constant temperature.

Instead of conducting distillation at constant temperature and varying pressure, the general practice is to conduct distillation at constant pressure. The boiling point of a solution is the temperature at which the total vapor pressure becomes equal to external pressure. The external pressure is frequently 1 atm. Thus, a solution of two components *A* and *B* will boil when the total pressure *i.e.*, P_A+P_B becomes equal to 1 atm. Since, according to Raoult's law, different compositions of a solution have different vapor pressures, it follows that solutions of different compositions will boil at different temperatures. Thus a solution whose components have higher vapor pressure will boil at a lower temperature than the solution in which the components have lower vapor pressures. This is because solutions of higher vapor pressures can reach the external pressure (1 atm) at relatively lower temperatures and start boiling than the solutions of lower vapor pressures.

Based upon this fact, it is possible to construct a boiling point diagram corresponding to vapor pressure diagram. Since there are three types of vapor pressure—composition diagrams, correspondingly we shall have three types of boiling point diagrams which are shown in Fig. 12.7.

Comparing the boiling point diagrams with the vapor pressure diagrams, we find that in boiling point diagrams, the *liquid curves are below the vapor pressure curves.* This can be readily explained because at constant pressure, the vapor state exists at the higher temperature.

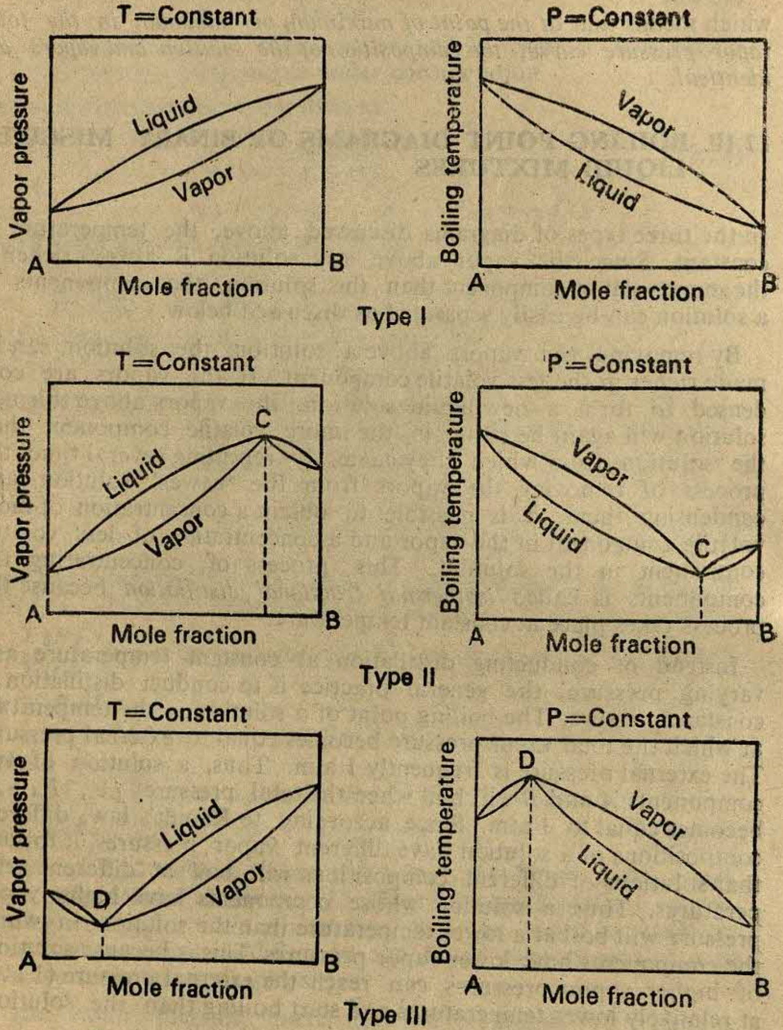


Fig. 12.7. Types of boiling point diagrams corresponding to various vapor pressures diagrams.

In type I, the vapor pressure of pure *A* is the lowest pressure and that of pure *B* is the highest while the vapor pressure of all possible compositions of *A* and *B* lie in between the two values, therefore, in the boiling point diagram, the boiling point of *A* is the highest and that of *B* is the lowest while the boiling points of all possible compositions of *A* and *B* lie in between the two values. The decrease in boiling point is regular from *A* to *B*.

Same arguments are also applied to the other two types. In type II, since the vapor pressure corresponding to the composition C is the highest, the solution corresponding to that composition will boil at the lowest temperature in the boiling point diagram. Similarly, in type III, since the solution of composition D has lowest vapor pressure, it will boil at the highest temperature in the boiling point diagram. Thus, we see that for any system the maxima in the vapor pressure diagram will be minima in the boiling point diagram and vice-versa.

12.11. FRACTIONAL DISTILLATION OF BINARY MISCIBLE LIQUID MIXTURES

Type I. System which is ideal

Consider the boiling point versus composition diagram for such a system which is shown in Fig. 12.8.

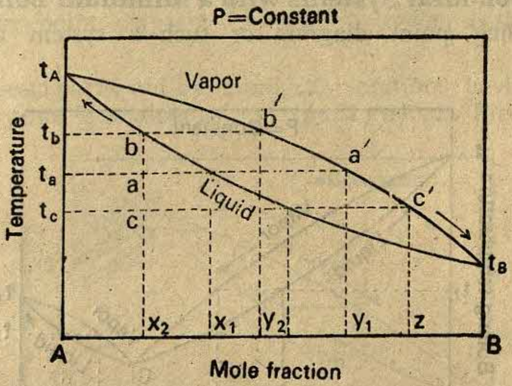


Fig. 12.8. Distillation behaviour of solutions of type I.

Suppose we heat a solution of composition X_1. The vapor pressure of the system will increase until it reaches the point a. At this point the vapor pressure of the solution becomes equal to the external pressure and hence the solution begins to boil. Thus t_a is the boiling point of the solution of composition X_1. At this temperature, the vapors coming off will have the composition Y_1, (point a' on the vapor composition curve). Since the vapors are richer in the more volatile component B, $(Y_1 > X_1)$, the residual liquid will become richer in the less volatile component A. Let it be represented by the point b on the liquid-composition curve. A solution of composition (X_2) will boil at temperature t_b which is higher than t_a. The corresponding composition of the vapors in equilibrium with solution of composition X_2 is given by Y_2, point b' on the vapor composition curve. These vapors are again richer in the component B and consequently the residual liquid will be further enriched in the component A. The temperature of this residual liquid must again be raised until it begins to boil. Thus we see that if the process described is continued several times, the residue will become richer and richer in *A* than the original solution until pure *A* is obtained. The boiling point will also increase continuously from t_a to t_A, the boiling point of the pure component *A*.

Consider now the vapor phase. If the initial vapors obtained from the solution (point a') as pointed out earlier, are condensed and redistilled, the vapors of composition *Z* (represented by the point c') are obtained and the boiling point of the new solution will be t_c. This shows that the distillate becomes richer in the component *B* than the original. When the process is repeated several times, a stage comes when the distillate is composed of pure *B* only.

Thus we see that by carrying out fractional distillation of mixtures which are ideal, it is possible to separate the two constituents into the pure components.

Type II. Non-ideal Systems with a Minimum Boiling Point

The boiling point diagram for such a system is shown in Fig. 12.9.

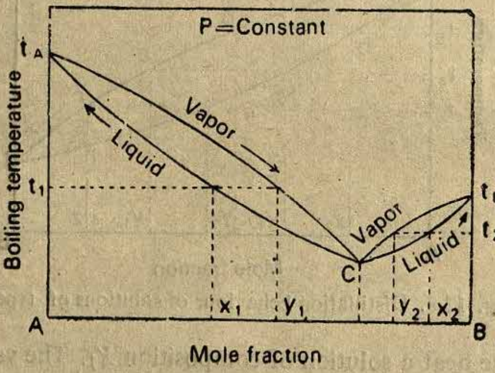


Fig. 12.9. Distillation behaviour of solutions of type II.

Consider the distillation of a solution of composition, say X_1, between *A* and *C*. This solution will boil at a temperature t_1 and the vapors in equilibrium with this solution at this temperature have the composition Y_1 and consequently will be richer in *B* than the residue. As the distillation proceeds, the composition of residual liquid will shift towards pure *A* and the boiling temperature of the residual liquid will also increase because it is richer in the less volatile constituent. On the other hand, the composition of the distillate will shift towards *C*. By repeating the process of condensation and distillation several times, as discussed in type I, eventually a stage is reached when the residual liquid will contain only pure liquid *A* and a vapor of composition *C* in the distillate at the minimum boiling point. When a vapor corresponding to composition *C* is condensed and distilled, it will yield again a vapor of composition *C*. This means that the vapors coming off from the solution at *C* will have the same composition as the solution and no further separation is possible. Thus a solution having composition between *A* and *C* can be separated by fractional distillation into pure *A* in the residue and a constant boiling mixture of composition *C* in the distillate. There will be no pure *B*.

Similar conclusion is reached if a solution of composition, say X_2, is heated between *B* and *C*. The vapors coming off will be richer in component *A* than the liquid residue. If the distillation is repeated, the distillate and the residue will become richer and richer in a constant boiling mixture and pure *B* respectively. Eventually, the distillation will yield pure *B* in the residue and a constant boiling mixture *C* in the distillate. There will be no pure *A*.

Type III. Non-ideal Systems with a Maximum Boiling Point

The boiling point diagram for such a system is shown in Fig. 12.10.

The behaviour borne out by non-ideal solutions having a maximum boiling point is analogous to type II systems. From reasoning analogous to type II, repeated distillation of a solution having composition between *A* and *D* will eventually yield pure *A* in the distillate and a constant boiling mixture *D* in the residue. There will be no pure *B*. Similarly, repeated distillation of a solution having composition between *B* and *D* will eventually yield pure *B* in the distillate and a constant boiling mixture *D* in the residue. There will be no pure *A*.

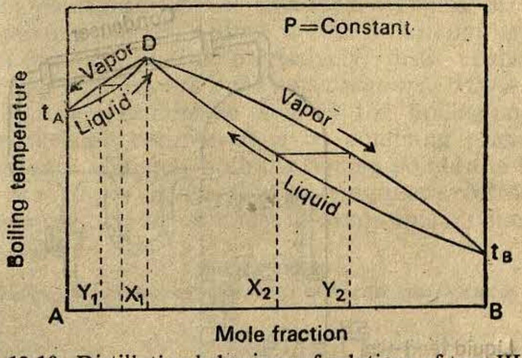


Fig. 12.10. Distillation behaviour of solutions of type III.

Thus we see that only ideal solutions can be separated by fractional distillation into the pure constituents. The separation into pure constituents is never possible for non-ideal systems showing positive or negative deviations from ideal behaviour.

12.12. THE FRACTIONATING COLUMN

The process of fractional distillation will be extremely tedious and involve more time and labour as the separation is carried out in batches and in discontinuous manner. To overcome these difficulties, a fractionating column is used. A fractionating column is a device which automatically carries out fractional distillation in a continuous manner. There are various types of fractionating columns, the most generally used in the laboratory is a "bubble-cap" type of column as shown in Fig. 12.11. The column which consists of a number of bubble-cap plates is attached to a boiler at the bottom and to a condenser at the top. Each plate can hold a thin layer of liquid. Liquid can flow down from one plate to the next by a series of overflow pipes and the vapor can rise and escape through several bubble caps *C*. The vapors moving upward through the caps prevent the liquid descending through them. To understand the working, the liquid mixture to be separated is boiled by heating coils in the boiler at the bottom. The vapors after passing through the caps come into contact and mix with the liquid at the plate 1. Some of the vapors of the less volatile component will condense here and the remaining vapors, richer in the more volatile component, will pass on through caps to plate 2. Here they will again come into contact and mix with the liquid at plate 2.

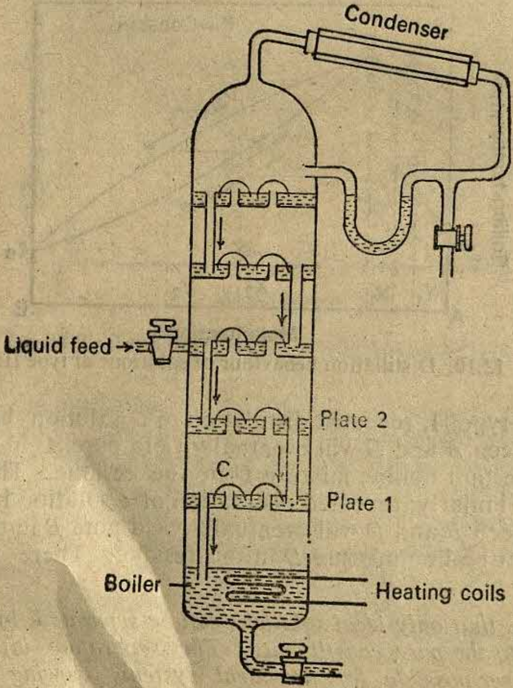


Fig. 12.11. Schematic diagram of bubble-cap fractionating column.

This will cause vapors of the volatile component to condense and vapors of the more volatile component move upwards. On repeating this process at every plate, the vapors moving upwards become increasingly enriched in the more volatile component and the liquid flowing down through the column becomes richer in the less volatile component. Thus the more volatile component can be drawn off in the pure form by condensing the vapors at the top of the column and less volatile component from the bottom.

In order to make the separation process continuous, the preheated liquid mixture is admitted into one of the plates at an intermediate stage in the column and the two pure liquids are drawn off from the top and bottom of the column. As the vapors from the boiler move up the column, they come into contact with the cooler liquid moving downward and there is a continuous condensation-vaporization exchange between the vapor and liquid phases at each plate in the column. Finally, vapors of the more volatile component are collected at the top and condensed to get the pure liquid and less volatile component collected at the bottom. It should be remembered that the complete separation in the pure form of the two components is possible only for an ideal system.

12.13. AZEOTROPIC MIXTURES

In the boiling point diagrams of non-ideal systems of type 2 and type 3, the mixtures corresponding to the minimum and maximum boiling point (points *C* and *D* respectively) distil unchanged. Such constant boiling mixtures are known as *azeotropic mixtures* or simply *azeotropes*. The compositions as well as the boiling points of azeotropes are remarkably constant at given confining pressure. But as the total pressure changes, both the boiling points and the compositions of the azeotropes change, thus proving that azeotropes are not definite compounds. Some examples of azeotropic mixtures are given in the Table 12.3.

TABLE 12.3.
Boiling points and compositions of azeotropic mixtures

(P=1 Atm)

Type	*Component A*	*B.P. °C*	*Component B*	*B.P. °C*	*Azeotrope*	
					Weight % A	*BP °C*
Minimum Boiling Point	Water	100	Ethyl Alcohol	78.3	4.0	78.174
	Water	100	Ethyl Acctate	79.6	11.3	73.41
	Carbon tetrachloride	76.75	Methyl Alcohol	64.7	79.49	55.7
	Chloroform	61.2	Methyl Alcohol	64.7	87.4	53.43
Maximum Boiling Point	Water	100	Nitric Acid	86	68	120.5
	Water	100	Hydrochloric Acid	80	20.222	108.584
	Chloroform	61.2	Acetone	56.10	78.5	64.43
	Phenol	182.2	Aniline	184.35	42	186.2

TABLE 12.4.

Effect of pressure on composition and boiling point of azeotropes

Pressure, mm	*Weight % of HCl in constant boiling mixture*	*B.P.° C*
800	20.155	110.007
760	20.222	108.584
700	20.360	106.424
500	20.916	97.578

12.14. COMPLETELY IMMISCIBLE LIQUIDS : STEAM DISTILLATION

Truly speaking no two liquids are completely insoluble in each other. However, there are certain liquid pairs *e.g.*, watar-mercury and water-carbon disulphide in which the mutual solubility is so small that they are considered to be completely immiscible. In a mixture of immiscible liquids, since two liquids are mutually insoluble, each liquid behaves as if the other were not present. Hence in a mixture of two immiscible liquids, each liquid will exert its own vapor pressure corresponding to the pure state at the given temperature independent of the other and the total vapor pressure, P, above the mixture will be the sum of the vapor pressures of the two pure liquids at that temperature. Thus if $P°_A$ and $P°_B$ are the vapor pressures of the two pure components, which are completely immiscible at a certain temperature, then the total pressure, P, is given by :

$$P=P°_A+P°_B$$

Again the boiling point of any system is the temperature at which the total vapor pressure of the system becomes equal to the external pressure. Thus a mixture of two immiscible liquids will boil, that is, distil freely. at a temperature lower than the normal boiling points of the two liquids taken separately because the two liquids together can reach the given external pressure at some lower temperature than either liquid alone. For example, at an external pressure of 734 mm, the boiling points of water and chlorobenzene are 99°C and 131°C respectively, but the boiling point of the mixture of the two liquids is 91°C at the same external pressure. Moreover, since at any given temperature, the total vapor pressure is independent of the relative amounts of the two liquids, the boiling point of the mixture must remain constant as long as both llquids are present. But as soon as one of the more volatile liquids is boiled away, the boiling temperature will rise abruptly from that of the mixture to that of the less volatile liquid.

In order to show that the weights of the two components distilled from an immiscible liquid mixture are proportional to their respective molecular weights and vapor pressure, we proceed as follows:

If Y_A and Y_B are the mole fractions in the vapor and $P_A{}^\circ$ and $P_B{}^\circ$ are the partial pressures of the components A and B respectively at any boiling temperature, T, for the mixture, then, according to Dalton's Law of partial pressures:

$$P^\circ{}_A = Y_A P \text{ and } P^\circ{}_B = Y_B P \qquad \ldots (12.28)$$

where P is the total pressure. Here assumption is made that vapors behave ideally. The ratio of the two expressions is given by:

$$\frac{P^\circ{}_A}{P^\circ{}_B} = \frac{Y_A}{Y_B} \qquad \ldots (12.29)$$

Again, since $$Y_A = \frac{n_A}{n_A + n_B}$$

and $$Y_B = \frac{n_B}{n_A + n_B}$$

where n_A and n_B are the number of moles of the components A and B, in the vapor.

Therefore,

$$\frac{P^\circ{}_A}{P^\circ{}_B} = \frac{n_A/(n_A+n_B)}{n_B/(n_A+n_B)} = \frac{n_A}{n_B} \qquad \ldots (12.30)$$

Since the temperature is constant, $P^\circ{}_A/P^\circ{}_B$ is constant and consequently, n_A/n_B must also be constant *i.e.*, the composition of the vapors above the binary mixture is always constant. Further, since the number of moles of any component is given by the ratio of the weight and molecular weight of that component,

$$n_A = \frac{W_A}{M_A} \text{ and } n_B = \frac{W_B}{M_B}$$

where W and M stand for the weight and the molecular weight of the respective constituent. Therefore, equation (12.30) becomes:

$$P^\circ{}_A/P^\circ{}_B = \frac{W_A M_B}{W_B M_A}$$

or $$\frac{W_A}{W_B} = \frac{M_A P^\circ{}_A}{M_B P^\circ{}_B} \qquad \ldots (12.31)$$

Equation (12.31) relates the relative weights of the two components in the distillate to their molecular weights and vapor pressures. If these vapors were condensed, equation (12.31) would give the relative weights of the two components in the condensate.

The process of distillation of immiscible liquids is generally utilised in the laboratory and in the industry for the purification of those liquids which boil at too high a temperature or which decompose when heated to their normal boiling points. When water is used as the other liquid, the whole process is referred to as steam distillation.

The immiscible mixture of the liquid to be purified and water is heated either directly or by passing steam through it. Generally, heating by bubbling steam through the system is preferred because it keeps the system agitating and equilibrium between the vapors and the two liquids is rapidly attained. The vapors distilling are condensed and separated in the pure forms. Thus, it is possible to distil many liquids of high boiling points at temperatures below the boiling point of water.

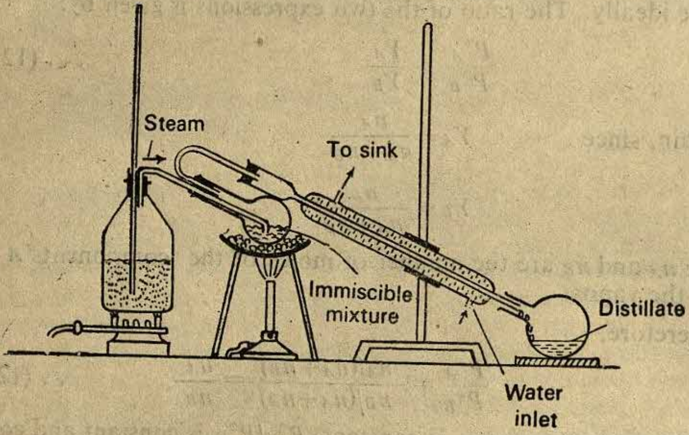


Fig. 12.12. Apparatus for steam distillation.

Consider for example, the purification of aniline. It has a boiling point of 180°C. But when aniline is heated with water with which it is immiscible by passing steam into it, it can be made to boil at a much lower temperature. The distillation takes place at 98.5°C which is lower than the boiling point of either aniline or water. Equation (12.31) can also be utilised to determine the approximate molecular weight of one of the liquids involved in the distillation. If the vapor pressures and the weight ratios of the steam distillate of the two components are known, and molecular weight of one of the liquids is known, molecular weight of the other liquid can be readily determined.

Problem 12.3. The hydrocarbon terpinene was found to distil freely in steam at a temperature of 95°C when the atmospheric pressure was 744 mm. The vapor pressure of pure water at this temperature is 634 mm The distillate contained . 55 per cent by weight of terpinene, calculate its molecular weight.

Solution If the terpinene is designated by *A*, and the water by *B*, it follows that at 95°C; the boiling point of the mixture, P_B° is 634 mm, and hence P_A° is equal to $P-P_B^\circ$ *i.e.* $744-634=110$ mm. The ratio W_A/W_B in equation (12.31) is 55/45, since the distillate contains 55 per cent of terpinene (*A*) and 45 per cent of water (*B*). It follows, therefore, from equation (12.31) that:

$$55/45 = \frac{110/M_A}{634 \times 18}$$

or

$$M_A = \frac{634 \times 18 \times 55}{45 \times 110}$$

∴ Molecular weight of hydrocarbon terpinene = 127.

12.15. PARTIALLY MISCIBLE LIQUID PAIRS

Liquids, which are partially miscible, form solutions which considerably deviate from ideal behaviour. Partially miscible liquid pairs dissolve in each other only in certain limits. Thus in the case of system phenol and water which are only partially miscible, phenol will completely dissolve in a large quantity of water to form a solution of phenol in water. If the quantity of phenol is gradually increased, a stage is reached when a saturated solution of phenol in water is formed. Further addition of phenol to water will result in the formation of two liquid layers, one a saturated solution of phenol in water and the other a saturated solution of water in phenol. Similarly, water will completely dissolve in a high proportion of phenol to form a solution of water in phenol. Thus, with high proportions of one of the two liquids, it is possible to have a completely miscible solution. But if the proportions taken exceed the saturation limits, two liquid layers are formed. The two liquid layers in equilibrium are known as *conjugate solutions* and will have the same vapor pressures. It has been observed that at constant pressure, the mutual solubility of two liquids changes with temperature. The three types of liquid pairs, which are obtained in actual practice, are (*i*) with increasing mutual solubility. (*ii*) with decreasing mutual solubility, and (*iii*) with closed mutual solubility.

1. Type with Increasing Mutual Solubility

Consider the case of phenol and water. These two liquids are partially miscible and form two liquid layers when their proportions. are taken outside the saturation limits. The lower layer will consist of a small amount of water dissolved in phenol and the upper layer will consist of a small amount of phenol in water. At a given temperature, the compositions of the two layers in equilibrium with each other are definite and can be determined experimentally. As long as two layers are present together and temperature is constant, there will be no change in the compositions of the two layers. The addition of small quantities of either phenol or water will merely change the relative volumes of the two layers and not their compositions. On increasing the temperature, the mutual solubility of two liquids in the two layers increases until at a certain temperature, the compositions of the two layers become the same. Beyond this temperature, the two liquids are completely miscible. This temperature, at which the two partially miscible liquids first become completely miscible, is known as the *critical solution temperature* (CST) or *consolute temperature* of the system. The composition corresponding to CST is known as critical composition. Above this temperature, the two liquids are miscible in all proportions and thus one layer is possible. In the case of phenol-water system, the critical solution temperature is 68.9°C.

The variation of mutual solubility of water and phenol with temperature is shown in Fig. 22.13.

The curve is more or less of the shape of a parabola. At any definite temperature, the compositions of the conjugate solutions are given by points on opposite branches of parabola. Thus, at a temperature *t*, the tie line *AB* gives the compositions of the conjugate solutions; point *A* represents composition of water rich layer and point *B* represents the composition of phenol rich layer. Between *A* and *B*, all mixtures yield two layers of composition *A* and *B*. If *X* represents a system of two layers whose relative compositions are given by *A* and *B* respectively, the relative weights of the two layers are given by the lever rule, according to which:

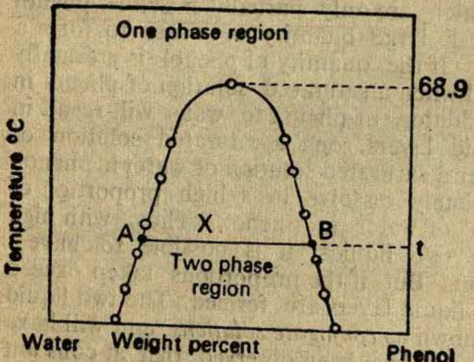


Fig. 12.13. Mutual solubility of water and phenol at various temperatures.

$$\frac{\text{weight of phenol layer}}{\text{weight of water layer}} = \frac{\text{distance } XA}{\text{distance } XB}$$

Outside the points *A* and *B*, two liquids are mutually soluble.

As the temperature is raised, the compositions of the two conjugate solutions gradually approach each other. This is due to the fact that the mutual solubility of the two liquids increases with rise of temperature. At the critical solution temperature (point *C* which is maximum of the curve), the two compositions become identical and the two layers merge into a single layer. Thus within the parabola, the system is heterogeneous and represents the range of existence of two liquid layers. Outside this parabola, the system is homogeneous and there is only a single liquid layer. Other examples of systems with upper critical solution temperature are:

Water-Aniline	(167°C)
Aniline-Hexane	(59.6°C)
Benzene-Sulphur	(163°C)
Methyl alcohol-cyclohexane	(49.1°C)
Methyl alcohol-carbon disulphide	(40.5°C)

2. Type with Decreasing Mutual Solubility

There are certain systems in which the mutual solubility decreases with increasing temperature. For such systems, the shape of the curve is reverse to type 1 and a lower critical solution temperature is observed. A schematic diagram for the system triethylamine-water is shown in Fig. 12.14.

As the curve indicates, the mutual solubility of water and triethylamine increases with decrease of temperature. At a temperature of 18.5°C(lower consolute temperature) and below, the two liquids are completely miscible. The composition of the solution corresponding to the critical solution temperature is found to be 30% by weight of triethylamine.

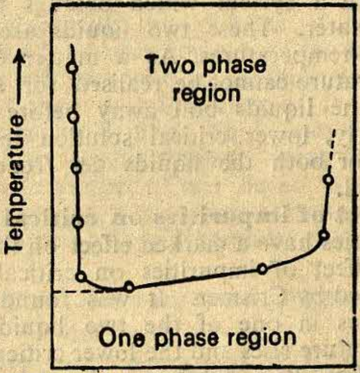


Fig. 12.14. Mutual solubility of water and triethylamine at various temperatures.

3. Type with Closed Mutual Solubility

In some systems, both upper and lower critical solution temperatures are exhibited. For such a system, there is a closed solubility curve. A schematic diagram for the system nicotine-water which belongs to this class is shown in Fig. 12.15.

For this system, the upper critical solution temperature is 208°C and the lower critical solution temperature is 60.8°C. Within these two temperatures in the enclosed area, the two liquids are partially miscible but outside them, they are completely miscible It was also found that the compositions corresponding to the two critical solution temperatures are same (34 per cent by weight of nicotine).

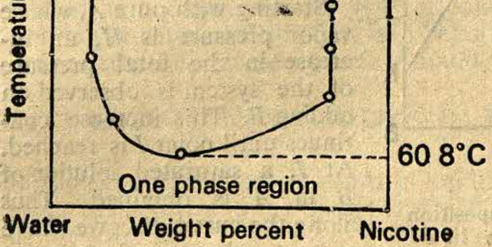


Fig. 12.15. Solubility of nicotine in water at various temperatures.

It has also been observed that when external pressure is applied to this, the lower critical solution temperature rises and the upper critical solution temperature decreases. Thus the area of closed ring becomes smaller and smaller with increase of pressure until finally a pressure is reached at which it becomes a point and the two liquids are completely miscible.

Type Without Critical Solution Temperature

There are some systems which do not exhibit either an upper critical solution or a lower critical solution temperature. An example of such a system which belongs to this type is the system ethyl ether-water. These two liquids are, therefore, partially miscible at all temperatures. As a matter of fact, upper critical solution temperature cannot be realised for such systems in which one or both the liquids boil away before that temperature is reached. Similarly, lower critical solution temperature cannot be recorded if one or both the liquids get frozen before that temperature is reached.

Effect of impurities on critical solution temperature. The impurities have a marked effect on the critical solution temperature. The effect of impurities on critical solution temperature was first observed by Crismer. It was found by him that if a substance dissolves in one of the two liquids, the upper critical solution temperature rises and the lower critical solution temperature decreases further. If a substance dissolves in both the liquids, the upper critical solution temperature will be lowered and the lower critical solution temperature will rise.

The critical solution temperature is so sensitive to minute traces of impurities that it can be used as a criterion of purity. Actually critical solution temperature is a linear function of the concentration of impurities.

12.16. VAPOR PRESSURE CURVES AND DISTILLATION PARTIALLY MISCIBLE LIQUID PAIRS

Consider two liquids *A* and *B* which constitute a partially miscible liquid pair. The vapor pressure composition diagram for such a system is shown in Fig. 12.16.

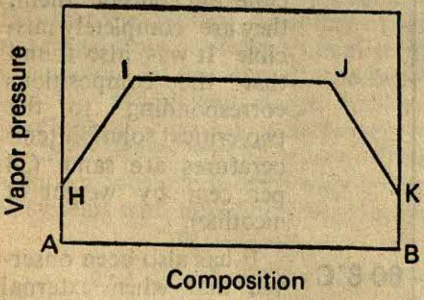


Fig. 12.16. Vapor pressure-composition diagram of partially miscible liquid pairs.

Starting with pure *A*, whose vapor pressure is *H*, an increase in the total pressure of the system is observed on adding *B*. This increase continues until point *I* is reached. At *I*, a saturated solution of *B* in *A* is obtained. Thus along the curve *HI*, we have a true solution of *B* in *A*. Similarly, starting with pure *B*, whose vapor pressure is *K*, an increase in the total pressure of the system is observed on adding *A*. This increase continues until point *J* is reached where a saturated solution of *A* in *B* is obtained. Thus along the curve *KJ*, we have a true solution of *A* in *B*. Since along the curves *HI* and *KJ*, only one liquid layer is present, there will be two phases (one liquid phase and the other vapor phase). In this case, application of phase rule gives:

$$F=C-P+2=2-2+2=2$$

which means the system is bivariant with two degrees of freedom. Thus the pressure will vary with composition even if the temperature is fixed or the temperature will vary with composition at a constant pressure. At points *I* and *J*, there is a formation of two liquid layers, one of *A* in *B* and the other of *B* in *A*. The vapor pressure corresponding to points *I* and *J* are exactly similar. Along the curve *IJ*, which represents the range of existence of two liquid layers, the total vapor pressure remains constant irrespective of composition. The same result can also be obtained by applying phase rule according to which:

$$F=C-P+2 \qquad \text{(There are two liquid phases and}$$
$$F=2-3+2=1 \qquad \text{one vapor phase.)}$$

i.e., the system is univariant having only one degree of freedom.

This means that only one of the variables, either pressure, temperature of composition, is sufficient to define the system completely. Thus as long as two liquid layers are present, irrespective of their relative amounts, the total vapor pressure of the system at a given temperature is constant.

The above facts can be utilised in carrying out distillation of partially miscible liquid pairs. When there is a single liquid layer, the boiling point of the mixture will vary with change in composition of the both liquid and vapor. Thus when such a mixture is distilled at a constant pressure, the less volatile component will be present in the liquid and the more volatile component in the vapor as in the case of completely miscibe liquid pairs.

When two layers are present, the system of all possible compositions between *I* and *J* will boil and distil over at a constant temperature and the composition of the vapor coming off as well as of distillate will also be constant. As soon as one of the two layers is used up completely, the boiling point will rise and the composition of the vapor and distillate will begin to change continuously as in the case of completely miscible liquid pairs.

12.17. SOLUTIONS OF SOLIDS IN LIQUIDS

In the case of solutions of solids in liquids, solid is always referred to as the solute and the liquid in which solid dissolves is referred to as the solvent.

If a solution contains at a given temperature as much solute as it can hold in the presence of the dissolving substance (solvent), it is said to be *unsaturated.* If the solution contains less than this amount of solute, it is said to be *unsaturated* and if contains more than this amount of solute, it is said to be *super-saturated.* The state of a solution with respect to saturation can be easily found by adding a small amount of the solute to the solution at some constant temperature. If the solute dissolves, the solution is unsaturated and if it does not dissolve, the solution is saturated. But if the precipitation starts, the solution is super-saturated. The super-saturated solution contains a larger percentage of the solute than a saturated solution at the same temperature although it is said that a saturated solution contains the largest possible proportion of the solute at the given temperature. In other words, super-saturated solution can be regarded as saturated solution plus excess solute. Super-saturated solution is unstable and can easily give up its solute.

"The amount of the solid which dissolves in 100 grams of the liquid at a particular temperature to give a saturated solution of it is known as the solubility of that solid in that particular solvent at that temperature."

The solubility depends on the nature of the solid and liquid, the temperature and to a much lesser extent on the pressure of the system. Thus at the same temperature, different substances will have different solubilities in the same solvent *e.g.*, at 20°C, the solubility of ammonium nitrate in water is 192 gms/100 gms while the solubility of mercuric chloride in the same solvent and at the same temperature is 6.5 gms/10 gms. On the other hand, the solubility of these substances in ethyl alcohol is 3.8 gms/100 gms and 47.6 gms/100 gms respectively. Generally, those substances which are soluble in water will not dissolve in other solvents and vice-versa. As a rule, inorganic substances are more soluble in water than in organic solvents while reverse is in the case of organic substances, although there are many exceptions to this rule.

The temperature has got a significant effect on the solubility of a solute in a particular solvent. For many salts, the solubility increases with rise in temperature but for some substances, the solubility decreases with rise in temperature *e.g.*, in the case of substances like ammonium chloride, lead nitrate, potassium chloride, potassium nitrate etc., the solubility increases with the rise in temperature while for substances like calcium acetate and calcium chromate, the solubility decreases with rise in temperature. As a matter of fact, the direction in which the solubility of a substance in a solvent changes with change of temperature depends on the heat of solution. If a substance dissolves at saturation with evolution of heat, the solubility decreases with rise in temperature. On the other hand, if the substances dissolve with absorption of heat, the solubility increases as the temperature rises. This is in accordance with the Le Chatelier Braun Principle. There are some substances in which the solubility first increases with rise in temperature, passes through a maximum and then begins to decrease with further increase in temperature *e.g.*, in the case of calcium sulfate, solubility increases up to 40°C, passes through a maximum at this temperature and then begins to decrease with further rise in temperature. Such substances are said to show *retrograde solubility*.

12.18. THE SOLUBILITY CURVE

The solubility curve is the curve drawn between the solubility and temperature. The solubility curve can take any of the two forms: (1) Continuous curve, and (2) Discontinuous curve.

As a rule, those substances which do not involve any change in the nature of the saturating solid phase, are said to have continuous solubility curve. This is shown in the curves for substances like lead nitrate, potassium nitrate, ammonium nitrate, ammonium chloride, sodium chloride, calcium acetate etc. (Fig. 12.17).

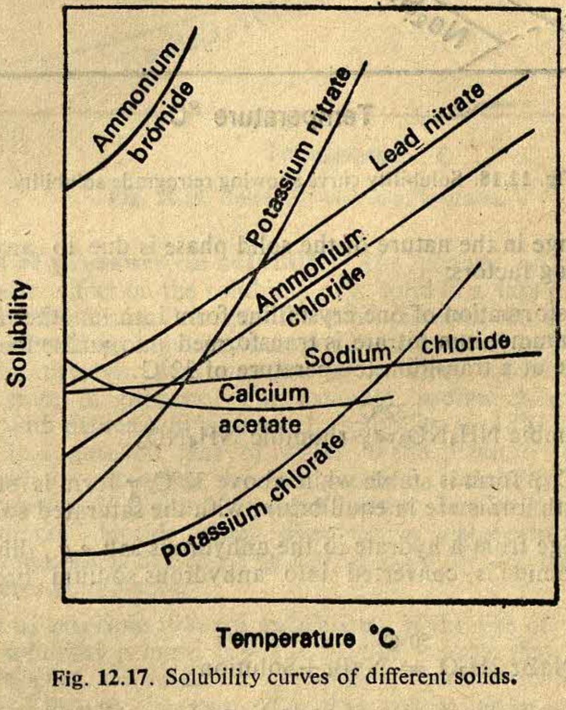


Fig. 12.17. Solubility curves of different solids.

On the other hand, for those substances which exhibit a change in the nature of the solid phase, a break appears in the solubility curve and the curve is discontinuous. The break in the solubility curve occurs at the point where the transition from one form to some new form takes place. The temperature corresponding to this point of break is known as the transition temperature and is fixed and characteristic of the solid involved (Fig. 12.18). Thus at the transition temperature, the original solid phase is in equilibrium with the new solid phase.

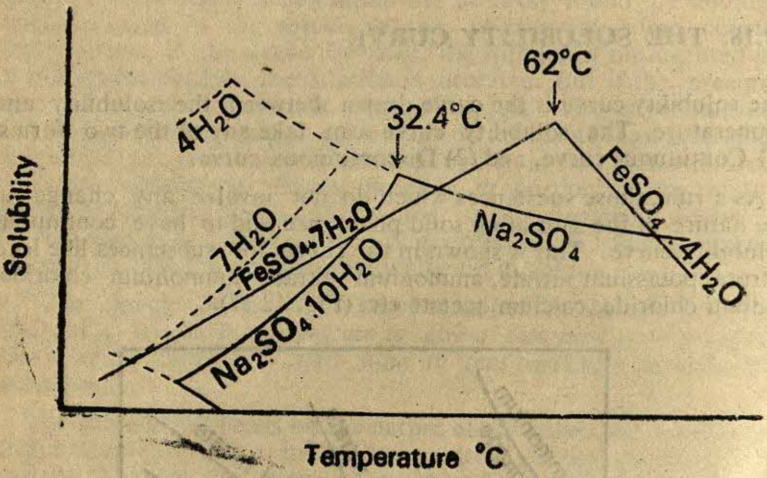


Fig. 12.18. Solubility curve showing retrograde solubility.

The change in the nature of the solid phase is due to any one of the following factors:

(1) Transformation of one crystalline form into another form *e.g.*, β-rhombic ammonium nitrate is transformed into γ-rhombic ammonium nitrate at a transition temperature of 32°C.

$$\beta\text{-rhombic } NH_4NO_3 \overset{32°C}{\rightleftharpoons} \gamma\text{-rhombic } NH_4NO_3$$

Below 32°C, β form is stable while above 32°C, γ form is stable and at 32°C, both forms are in equilibrium with the saturated solution.

(2) Change from a hydrate to the anhydrous salt *e.g.*, dihydrate of sodium bromide is converted into anhydrous sodium bromide at 50°C.

$$NaBr.2H_2O \overset{50°C}{\rightleftharpoons} NaBr + \text{Solution}$$

(3) Change in the degree of hydration of the solid in contact with the saturated solution *e.g.*, in the case of hydrated calcium chloride, the following transformations take place.

$$CaCl_2.6H_2O \overset{35°C}{\rightleftharpoons} CaCl_2.4H_2O$$

$$CaCl_2.4H_2O \overset{47°C}{\rightleftharpoons} CaCl_2.2H_2O$$

Similarly, in the case of sodium borate, we have:

$$Na_2B_4O_7.10H_2O \overset{61^\circ C}{\rightleftharpoons} Na_2B_4O_7.5H_2O$$

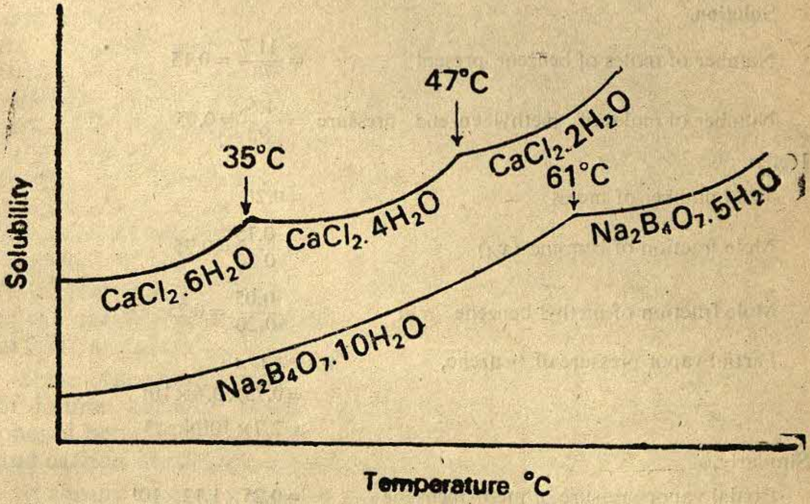


Fig. 12.19. Solubility curves of hydrates.

Effect of pressure on solubility. The change of pressure has got a little effect on the solubility of a solid in a liquid. According to Le-Chatelier Braun Principle, if a solid dissolves in a liquid with decrease of volume, solubility increases with increase of pressure and if the solid dissolves with increase of volume, solubility decreases with increase of pressure. For example, sodium chloride dissolves in water with decrease in volume. Its solubility at 18°C and 1 atmosphere is 26.4 gms/100 gms of water. If the pressure is increased to 500°C without changing the temperature, solubility of sodium chloride rises to 27.0 gms/100 gms of water. Similarly, in the case of ammonium chloride which dissolves in water with increase in volume, solubility is decreased by 5.1 per cent for a change of 500 atmospheres in pressure.

Effect of particle size on solubility. If the size of the particle is small, solubility is more. It is due to this reason that when solution is prepared, the solute is generally powdered to increase the solubility. Thus in the case of calcium sulfate, when its particles in the original size (2 micron) are dissolved in water at 18°C, its solubility is 2.085 gms/1000 gms of water. But when the size of the particle is reduced from 2 micron to 0.3 micron, the solubility rises to 2.476 gms/1000 gms of water at the same temperature. Similarly, in the case of barium sulfate, the solubility is almost doubled when the particle size of barium sulfate is decreased from 1.8 micron to 0.1 micron.

Problem 12.4. Calculate the vapor pressure over a solution containing 11.7 g benzene and 4.6 g methylbenzene at 50°C, if the vapor pressure of the pure components at this temperature are 3.6×10^4 Nm^{-2} and 1.12×10^4 Nm^{-2} respectively.

Solution.

Number of moles of benzene present $= \frac{11.7}{78} = 0.15$

Number of moles of methylbenzene pressure $= \frac{4.6}{92} = 0.05$

Hence,

Total number of moles $= 0.20$

Mole fraction of benzene (x_A) $= \frac{0.15}{0.20} = 0.75$

Mole fraction of methyl benzene (x_B) $= \frac{0.05}{0.20} = 0.25$

Partial vapor pressure of benzene, $p_A = x_A p_A^\circ$

$= 0.75 \times 3.6 \times 10^4$

$= 2.7 \times 10^4$Nm^{-2}

Similarly,

Partial vapor pressure of methylbenzene $= 0.25 \times 1.12 \times 10^4$

$= 0.28 \times 10^4$Nm^{-2}

Thus

Total vapor pressure of the mixture $= 2.98 \times 10^4$Nm^{-2}

12.19. DISTRIBUTION OF A SOLUTE BETWEEN TWO NON-MISCIBLE SOLVENTS (THE NERNST DISTRIBUTION LAW)

The law deals with the distribution of a solid between two non-miscible or partially miscible solvents in contact with each other. Consider, for example, the distribution of iodine between two non-miscible solvents—water and carbon tetrachloride. Iodine is soluble in both these solvents. When a known volume of a solution of iodine is shaken for a period of time with carbon tetrachloride, it is found that iodine distributes or divides itself between the water and carbon tetrachloride layers in such a manner that at equilibrium, the ratio of the concentrations of iodine in the two layers is constant at a given temperature and is independent of the actual amount of iodine present. If C_1 is the concentration of iodine in carbon tetrachloride layer and C_2 is its concentration in aqueous layer, then

$$\frac{C_1}{C_2} = K_D \qquad \ldots (12.32)$$

The constant K_D is known as the *distribution or partition coeffi-*

cient of the system and equation (12.32) is known as the Nernst Distribution Law. According to this law, a *dissolved substance, irrespective of its amount, distributes itself between two nonmiscible solvents in contact with each other in such a way that at equilibrium, the ratio of the concentrations of the substance in the two layers is constant at any given temparature.* Some results of the distribution of iodine between water and carbon tetrachloride at 20°C are given in Table 12.5.

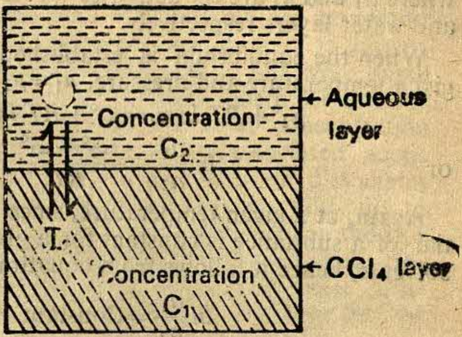


Fig. 12.20. Distribution of iodine between water and carbon tetrachloride.

Some other examples of the distribution law are the distribution of iodine between water and carbon disulphide or chloroform, phenol between water and amyl alcohol, bromine between water and carbon disulphide, succinic acid between water and ether etc.

It should be noted that the distribution law in the form of equation (12.32) is applicable only to dilute solutions or when the solute behaves ideally. For this reason, the dissolved substance should be sparingly soluble in the two solvents so that the saturated solutions are dilute.

TABLE 12.5.

Moles of I_2 per litre of CCl_4 (C_1)	*Moles of I_2 per litre of water* (C_2)	$K_D = \frac{C_1}{C_2}$
0.02	2.35×10^{-4}	85.1
0.04	4.69×10^{-4}	85.2
0.06	7.03×10^{-4}	85.4
0.08	9.30×10^{-4}	86.0
0.10	11.4×10^{-4}	87.5

12.20. THERMODYNAMIC DEDUCTION OF DISTRIBUTION LAW

Distribution Law can easily be deduced from thermodynamic considerations. Consider the distribution of iodine between water and carbon tetrachloride at some temperature, say T°C. If μ_1 is the chemical potential of iodine in carbon tetrachloride and μ_2 is its chemical potential in water, then

$$\mu_1 = \mu_1^\circ + RT \ln a_1$$

and

$$\mu_2 = \mu_2^\circ + RT \ln a_2 \qquad \ldots (12.33)$$

where a_1 and a_2 are the activities of iodine in carbon tetrachloride and water layers respectively.

When the equilibrium is established between the two layers at a given temperature and pressure, $\mu_1=\mu_2$ and hence it follows that

$$\mu_1^\circ+RT\ ln\ a_1=\mu_2^\circ+RT\ ln\ a_2$$

or

$$ln\frac{a_1}{a_2}=\frac{\mu_2^\circ-\mu_1^\circ}{RT} \qquad \ldots (12.34)$$

Again, at a given temperature, since the standard chemical potential of a substance is constant for a given substance in the particular solvents, hence it follows from equation (12.34) that

$$ln\frac{a_1}{a_2}=\text{Constant}$$

or

$$\frac{a_1}{a_2}=\text{Constant} \qquad \ldots (12.35)$$

which is the appropriate form of the distribution law. For systems which are ideal, the activity is almost equal to the concentration, hence equation (12.35) reduces to:

$$\frac{C_1}{C_2}=\text{Constant } (K_D)$$

which is in agreement with the simple form of the distribution law equation (12.32).

The distribution law is also applicable to the distribution of a solute between any two phases other than liquids such as gas-liquid, liquid-solid etc. Thus, in the Henry's Law, which deals with the solubility of a gas in a liquid, if the solution is very dilute, m, the mass of the gas in unit volume of the solution, is proportional to the concentration of the gas in the solution while the pressure p is proportional to $\frac{n}{V}$, the concentration in the gas phase. Thus the ratio $\frac{m}{p}$ is essentially the ratio of the concentrations of the gas between the two phases—liquid and gas and hence the Henry's law constant can be treated as distribution constant.

It was pointed out by Nernst that the distribution law given by equation (12.32) is valid only *when the dissolved substance has the same molecular form i.e., same molecular weight in both solvents.* If the solute does not have the same molecular weight in the two solvents, the simple form of the distribution law breaks altogether. Thus in a given non-miscible solvent pair, if the solute undergoes partial association in one of the solvents to form dimers and dissolves in the other solvent without any association or dissociation (no change in molecular form), the ratio of the concentrations of the solute in the two solvents, as given by equation (12.32), will not be constant. For such cases, the distribution law is applicable only to the ratio of the concentrations of the species having identical molecular weights in the two solvents.

Consider, for example, the distribution of acetic acid between water and benzene. In water, acetic acid exists mainly as monomers *i.e.*, as CH_3COOH. However, in benzene, acetic acid is largely associated to form dimers *i.e.*, $(CH_3COOH)_2$ with a relatively small proportion of single molecules. Now the partition coefficient for the distribution law will be given by the ratio of the total concentration of acetic acid in water and the concentration of unassociated acetic acid in benzene. Thus in general if a solute associates or dissociates in one or both the solvents, the distribution law will be valid only to the ratio of the concentrations of common species present in the two solvents and not to the ratio of the total concentration in the two solvents. For such cases, the distribution law can be obeyed satisfactorily if suitable modifications are made in the distribution law equation. This is done as given below:

Case I. *Correction for the association of the solute in one of the two solvents.*

Consider the solute represented by the molecular formula A. Suppose it exists as such in one solvent (marked as solvent I) in which its concentration is C_1 and in the other solvent (marked as solvent II) exists mainly as the associated molecules, $(A)_n$. Let the total concentration in the solvent II be C_2. The equilibrium between associated and simple molecules in solvent II is represented by

$$(A)_n \rightleftharpoons nA$$

Applying the law of mass action to this equilibrium and assuming the solution to be dilute, the equilibrium constant K_c is given by

$$K_c = \frac{C^n{}_A}{C_{(A)_n}} \qquad \ldots (12.36)$$

where C_A and $C_{(A)_n}$ are the concentrations of simple molecules and associated molecules respectively in solvent II.

Equation (12.36) can also be written as

$$C_A = \sqrt[n]{K_c \times C_{(A)_n}}$$

or

$$C_A = \text{Constant} \times \sqrt[n]{C_{(A)_n}} \qquad \ldots (12.37)$$

But since the solute exists mainly as the associated molecules, the concentration of the associated molecules can be taken as approximately equal to C_2 the total concentration in the solvent II. Equation (12.37) therefore, becomes

$$C_A \approx \text{constant} \times \sqrt[n]{C_2} \qquad \ldots (12.38)$$

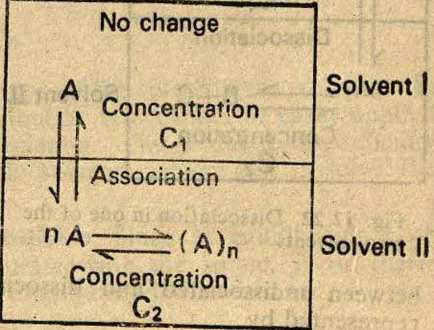


Fig. 12.21. Association in one of the two solvents.

Again, since the distribution law is valid only to the ratio of the concentrations of similar molecular species present in the two solvents, therefore,

$$\frac{C_1}{C_A} = \text{Constant} \qquad \ldots (12.39)$$

Substituting the value of C_A from equation (12.38) into equation (12.39) we get

$$\frac{C_1}{\sqrt[n]{C_2}} = \text{Constant} \qquad \ldots (12.40)$$

Equation (12.40) can be tested by applying it to study the distribution of benzoic acid between water and benzene. In this case, it is found that the ratio $\frac{C_1}{C_2}$ is not constant but $\frac{C_1}{\sqrt{C_2}}$ remains constant over a range of concentrations. This indicates that value of n in equation (12.40) is 2 and benzoic acid exists mainly as $(C_6H_5COOH)_2$ in benzene.

In order to know n, equation (12.40) is tried for different values of n on the experimental data. Taking logarithm of equation (12.40), we get

$$\log C_1 = \frac{1}{n} \log C_2 + \text{constant}$$

If a graph is plotted between $\log C_1$ and $\log C_2$, we should get a straight line with the slope equal to $\frac{1}{n}$.

Case II. *Correction for the dissociation of the solute in one of the two solvents.*

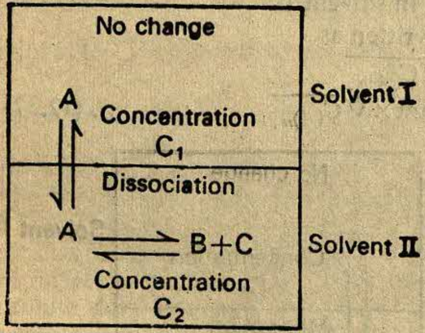


Fig. 12.22. Dissociation in one of the two solvents.

Consider again the solute represented by the molecular form A. Suppose it dissolves in solvent I without any change in the molecular form and dissociates into the species B and C in solvent II. Let C_1 be the concentration of undissociated molecules in solvent I and C_2 the total concentration in solvent II. In solvent II, if α is the degree of dissociation of the solute, the concentration of undissociated molecules will be $C_2(1-\alpha)$. The equilibrium between undissociated and dissociated molecules in solvent II is represented by

$$\begin{array}{ccccc} A & \rightleftharpoons & B & + & C \\ C_2(1-\alpha) & & C_2\alpha & & C_2\alpha \end{array}$$

Therefore, from distribution law,

$$\frac{C_1}{C_2(1-\alpha)}=\text{Constant.}$$

Similarly, if the solute is dissociated in both the solvents, distribution law becomes

$$\frac{C_1(1-\alpha_1)}{C_2(1-\alpha_2)}=\text{Constant}$$

where α_1 and α_2 are the degree of dissociation of the solute between solvent I and solvent II respectively.

12.21. APPLICATIONS OF THE DISTRIBUTION LAW

The distribution law has been successfully applied to the study of problems of both theoretical and practical interest. Some of its useful applications in physical chemistry are given below:

(*i*) **Study of association or dissociation of a solute in a solvent.** As discussed above, the distribution law can be employed as an important tool in deciding whether a solute is associated or dissociated in any particular solvent and to what extent association or dissociation of the solute takes place.

If a solute is associated in one of the solvents in which its concentration is C_2 and remains in its normal form in the other solvent where its concentration is C_1, then partition coefficient is given by

$$\frac{C_1}{\sqrt[n]{C_2}}=K_D$$

where n is the number of simple molecules which combine to form one associated molecule.

Similarly, if a solute is dissociated in one of the solvents in which its concentration is C_2 and does not undergo any change in the other solvent in which its concentration is C_1, then the partition coefficient is given by

$$\frac{C_1}{C_2(1-\alpha)}=K_D$$

where α is the degree of dissociation of the solute in the solvent. In the case of electrolytes, the distribution law cannot be easily applied to determine the degree of dissociation This is due to the difficulty in finding a pair of non-miscible solvents which can dissolve the electrolyte.

(*ii*) **Determination of solubilities**. Since at equilibrium, both the non-miscible solvents are saturated with the solute, it is, therefore, possible to write down the distribution law as follows:

$$\frac{C_1}{C_2}=\frac{S_1}{S_2}=K_D$$

where S_1 and S_2 are the saturation solubilities of the solute in the two solvents.

Thus, from a knowledge of partition coefficient, it is possible to determine the solubilities of a solute.

(*iii*) **Study of chemical equilibria leading to the formation of complex ion.** The distribution law can be successfully applied in determining the equilibrium constants of many reactions like the hydrolysis of chlorine ($H_2O+Cl_2 \rightleftharpoons HCl+HOCl$) and other salts, formation of complex, $Cu(NH_3)_4$, in ammonical solution of copper sulphate in water, the reaction between iodine and iodide ions etc. In such studies, the other solvent which is generally chosen is that which can dissolve one of the reactants or products such as benzene, carbon disulphide etc.

Consider, for example, the equilibrium given as below:

$$KI+I_2 \rightleftharpoons KI_3$$

or

$$I^-+I_2 \rightleftharpoons I_3^-$$

In order to determine the equilibrium constant of this reaction, first of all distribution coefficient (K_D) of iodine is determined by studying its distribution between carbon disulphide and water.

A solution of iodine in carbon disulphide is then shaken with an aqueous solution of potassium iodide so that iodine distributes itself between carbon disulphide layer and the aqueous layer. In the aqueous layer, iodine combines with potassium iodide to form a complex ion KI^-_3 as shown in Fig. 12.23.

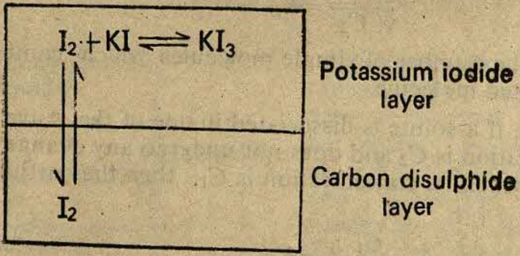


Fig. 12.23. Study of complex ions.

By knowing the concentration of iodine in the carbon disulphide layer at equilibrium and the distribution coefficient, concentration of free iodine in the potassium iodide solution can be easily calculated with the help of distribution law.

If the initial concentration of potassium iodide solution is given, then the concentration of I^- and I_3^- at equilibrium can also be calculated easily. The equilibrium constant for the reaction

$$I^-+I_2 \rightleftharpoons I_3^-$$

is then given by

$$K=\frac{]I_3^-]}{[I^-]\,[I_2]}$$

where all the terms in the brackets stand for the concentrations of various species involved.

(*iv*) **The process of extraction.** The distribution law finds numerous applications in the process of extraction of a solute from a solvent both in the laboratory and in industry.

In the laboratory, the process of extraction is utilized to separate a dissolved substance from a solution whereas the other methods such as distillation, etc., fail due to various reasons. This is done by shaking the solution containing the dissolved substance with some suitable solvent in which the required substance is more soluble and the solutions separated. The solvent is then easily removed by distillation. Similarly, in industry, extraction is used to purify various substances such as petroleum oils by treating the impure product with a suitable solvent in which the impurity is more soluble. Usually organic compounds are more soluble in organic solvents while inorganic substances are more soluble in polar solvents such as water. Thus when an organic substance is to be separated from an aqueous solution, the solution is shaken up with an appropriate organic solvent such as ether, benzene, chloroform etc., which is immiscible with water. The substance will distribute itself between the two layers (aqueous layer and organic layer) in such a way that a larger amount of it will remain in the organic layers. The two layers are then separated and water layer is again shaken up with more organic solvent. On repeating the process of extraction several times, it is possible to recover almost whole of the organic substance from the aqueous solution.

It can be easily shown that extraction is more economical and efficient if the given volume of the solvent is not used in one operation but is used in several instalments, each time separating the solvent. Suppose 100 ml of an aqueous solution contains A grams of succinic acid and 100 ml of the ether is available at our disposal for extraction. Let the distribution coefficient of succinic acid between ether and water is 5. If the entire 100 ml of ether is used for a single extraction, then W, the amount of succinic acid that passes into ethereal layer is given by the distribution law:

$$\frac{W/100}{\dfrac{A-W}{100}}=5$$

or

$$W=\frac{5}{6}A$$

i.e, only 83.3% of succinic acid is recovered.

On the other hand, if two successive extractions are made using

50 ml each time, then W_1, the amount of succinic acid that passes into the ethereal layer in the first extraction. is given by

$$\frac{\frac{W_1}{50}}{\frac{A-W_1}{100}}=5$$

or $$W_1=\frac{5}{7}A$$

i.e., 71.4% of succinic acid is recovered in the first extraction.

Similarly, W_2, the amount of succinic acid recovered in the secon extraction is given by

$$\frac{\frac{W_2}{50}}{\frac{(A-\frac{5}{7}A)-W_2}{100}}=5$$

or $$W_2=\frac{10}{49}A$$

i.e., 20.4% of succinic acid is recovered in the second extraction.

Thus we see that if 100 ml of ether is to be used for a single extraction, only 83.3% of succinic acid is recovered but if the same 100 ml of the ether is used in the two extractions, the amount of succinic acid extracted increases to 91.8%. It can be shown that if extraction is carried out 10 times, using 10 ml of ether each time, the amount of succinic acid recovered will be much more.

Hence, it can be generalised that the *process of extraction is much more complete and economical if it is carried out in several operations with a given volume of the solvent.*

Let us consider a solution containing W gms of a solute in V ml of the solution. Suppose this solution is repeatedly extracted with v' ml of pure immiscible solvent. Let W_1 is the weight of the solute left unextracted at the end of first extraction. Then the concentration of the solute in the original solution is W_1/V and $\frac{W-W_1}{v'}$ will be the concentration of the solute in the extracting liquid. If K_D is the distribution coefficient of the system, then according to the distribution law, assuming no complications of association or dissociation of the solute with the solvent,

$$\frac{W_1/V}{\frac{W-W_1}{v'}}=K_D \qquad \ldots (12.41)$$

Solving for W_1, one gets

$$W_1=W\left(\frac{K_DV}{K_DV+v'}\right) \qquad \ldots (12.42)$$

Similarly, W_2 the weight of the solute left in the original solution at the end of the second extraction with the same quantity of the solvent is given by

$$W_2 = W_1\left(\frac{K_D V}{K_D V + v'}\right) \qquad \ldots (12.43)$$

Substituting the value of W_1 from equation (12.42) into equation (12.43), one gets

$$W_2 = W\left(\frac{K_D V}{K_D V + v'}\right)^2 \qquad \ldots (12.44)$$

Similarly, at the end of n extractions, the weight of the solute W_n, left unextracted is given by

$$W_n = W\left(\frac{K_D V}{K_D V + v'}\right)^n \qquad \ldots (12.45)$$

If on the other hand, all the extracting solvent had been used in a single operation, then

$$\frac{\dfrac{W_n}{V}}{\dfrac{W - W_n}{nv'}} = K_D$$

or

$$W_n = W\left(\frac{K_D V}{K_D V + nv'}\right) \qquad \ldots (12.46)$$

In equation (12.46), since the quantities K_D, V and W are constants for a given system, the magnitude of W_n will depend on v' and n. In order to attain a greater extracting efficiency with the given volume of the solvent, W_n must be as small as possible. This can be possible by keeping v' small and n large, rather than the reverse. In other words for a given volume of extracting solvent, it is always more economical and efficient to carry out extraction in portions with small amounts of the solvent, rather than using all the solvent in a single extraction.

In the Parke's process for the recovery of silver from argentiferous lead, molten zinc is added in instalments to molten argentiferous lead. Silver present in the argentiferous lead distributes itself between lead and zinc and two immiscible layers are formed. Since the partition coefficient of silver is 300 times more in zinc than in lead, more of silver will pass into the zinc layer which is separated. If this process is repeated several times, practically all the silver passes into the zinc layer from which it can be easily recovered. The same principle can be applied to washing of precipitates in which case the distribution of impurity takes place between wash liquid and the precipitate.

Problem. 12.5. The distribution ratio of iodine between carbon disulphide and water is found to be 625. When iodine is distributed between carbon disulphide and a 0.125 molar solution of KI, the concentration of iodine in the former layer is found to be 0.1896 mole per litre, the total concentration in the aqueous KI layer is 0.02832 mole per litre. What is the concentration of I^-_3 ion in the latter layer?

Solution. The concentration of free I_2 in the KI layer must be equal to the concentration in the carbon disulphide divided by the distribution ratio for free iodine *i.e.* 0.1896/625 mole per litre; hence

Conc. of I_2 in KI layer$=\dfrac{0.1896}{625}=0.000303$ mole per litre. The total concentration of iodine in this layer is 0.02832 molar, and so the concentration of I^-_3 ions is

$$0.02832-0.000303=0.028017 \text{ mol per litre.}$$

Problem 12.6. An aqueous solution contains 0.20 g aspirin ($C_9H_8O_4$) in a 50 ml solution. To this solution is added 20 ml of ether, and the mixture is shaken and allowed to come to equilibrium at 25°C. At this temperature

$K_D=\dfrac{C_{ether}}{C_{H_2O}}=4.7.$ (*a*) How much aspirin remains in the aqueous phase?

(*b*) If the extraction is carried out with two successive 10 ml portions of ether, how much aspirin remains unextracted?

Solution. (*a*) The aqueous solution originally contained 0.20 g/180=0.00111 mole aspirin. Let x be the number of moles of aspirin extracted by 20 ml ether. Then, from equation (12.32)

$$\mathrm{K_D}=\frac{C_{Ether}}{C_{H_2O}}=\frac{\dfrac{x}{20}}{\dfrac{(0.00111-x)}{50}}=4.7$$

which gives $x=0.00073$, the number of moles of aspirin extracted. Therefore, $(0.00111-0.00073)=0.00038$ moles of aspirin remain in the water solution.

(*b*) Let y is the number of moles of aspirin extracted with the first 10 ml portion of ether. Then, as in part (*a*),

$$\frac{\dfrac{y}{10}}{\dfrac{0.00111-y}{50}}=4.7$$

which gives $y=0.00054$ mole of aspirin extracted. Therefore, $(0.00111-0.00054)$ $=0.00057$ mole of aspirin remains in the water solution. Again if z is the number of moles extracted with the second of 10 ml portion, then,

$$\frac{\dfrac{z}{10}}{\dfrac{(0.00057-z)}{50}}=4.7$$

which gives $z=0.00028$ mole of aspirin extracted. Finally, the amount of aspirin remaining unextracted is 0.00029 mole. A comparison of the results in (*a*) and (*b*) shows that the extraction with two successive 10 ml portions is more efficient than is in a single extraction with the whole 20 ml.

PROBLEMS

1. Define and explain the term 'solution'. What are the different ways of expressing the concentration of a solution?

2. State and explain Henry's Law. In an ideal dilute solution, if p° is the vapor pressure of the solvent and K_h is the Henry's Law constant for the solute, write the expression for the total pressure over the solution as a function of x, the mole fraction of the solute.

3. Suppose that the vapor over an ideal solution contains n_1 moles of 1 and n_2 moles of 2 and occupies a volume V under the pressure $p=p_1+p_2$. If we define $\overline{V}_2^\circ=RT/p_2^\circ$ and $\overline{V}_1^\circ=RT/P^\circ_1$, show that Raoult's law implies $V=n_1\overline{V}_1^\circ+n_2\overline{V}_2^\circ$.

4. Benzene and toluence form nearly ideal solutions. If at 300K, $p^\circ_{toluene}=32.06$ mm and $p^\circ_{benzene}=103.01$ mm.

(*a*) compute the vapor pressure of a solution containing 0.60 mole fraction toluene.

(*b*) calculate the mole fraction of toluene in the vapor for this composition of liquid.

Ans. (*a*) 60.40 mm (*b*) 0.318).

5. A mixture of $C_6H_5CH_3$ and C_6H_6 contains 30% by weight of $C_6H_5CH_3$. At 30°C, the vapor pressure of pure $C_6H_5CH_3$ is 36.7 mm Hg while that of pure C_6H_6 is 118.2 mm. Assuming that the two liquids form ideal solutions, calculate the total pressure and the partial pressure of each constituent above the solution at 30°C.

Ans. $P_{C_6H_6}=86.7$ mm; $P_{total}=96.5$ mm

6. Explain the terms "upper consolute temperature" and "lower consolute temperature." Discuss the variation of mutual solubility of nicotine and water with temperature.

7. Konovaloff's rule states: "The vapor in equilibrium with a binary liquid mixture is richer in that component whose addition to the liquid mixture (at constant temperature) increases the total vapor pressure." Discuss whether this rule applies to the boiling point versus composition diagrams exhibiting a maximum or a minimum. Does the rule apply to the azeotropic mixtures?

8. Discuss the principle of

(*i*) Steam distillation;

(*ii*) Fractional distillation of a miscible liquid pair.

9. An organic liquid which is immiscible with water is steam distilled at 80°C and at 751 mm Hg. The distillate is found to contain 71 per cent by weight of the organic liquid. The vapor pressure of water at 80°C is 355 mm Hg. Calculate the molecular weight of the organic liquid.

Ans. 39.54

10. Chlorobenzene (112 g/mol) is steam distilled at 734 mm at 90°C. The vapor pressure of chlorobenzene and steam at 90°C are 208 and 526 mm respectively. Calculate the weight of steam required to distil 500 gms of chlorobenzene.

Ans. 203 g.

11. Calculate the mole fraction, molal and molar concentrations of a solution containing 24 per cent acetic acid by weight in water, if the density of the solution at 20°C is 1.026 g/ml.

Ans. $X_2=0.0697$; m=4.16; M=3.4.

12. The Bunsen absorption coefficient of oxygen in water at 19.94°C is 0.03097 atm^{-1}. How many moles of oxygen from air (21 per cent by volume O_2, 79 per cent by volume N_2) at a total pressure of 1 atm could be dissolved in 1 litre of water at that temperature?

Ans. 0.000290 moles O_2 dissolved per litre water.

13. At 30°C, 244.0 ml of water dissolved 2.265 ml of helium (measured at 30°C and 1 atm). Evaluate α, the Bunsen absorption coefficient, for helium at this temperature.

Ans. 0.00836.

14. State Nernst Distribution law. Derive an expression for determining the degree of association of a substance, which undergoes association in one of the two liquids.

15. On shaking various amount of I_2 with CCl_4 and H_2O mixture, the concentration of I_2 in the two layers was found to be:

Conc^n of I_2 in CCl_4	6.12	12.24	15.2	22.38
Conc^n of I_2 in H_2O	0.072	0.143	0.178	0.260

Calculate the value of partition coefficient.

Ans. 85.0, 85.6, 85.2, 86.1.

16. (*a*) Deduce the general expression for extraction of a solid from solutions of *v* c.c. each.

(*b*) A volume of 50 ml of aqueous solution of iodine containing 4 mg of Iodine is shaken with 10 ml of CCl_4 which is allowed to separate. (*a*) Calculate the quantity of iodine left behind in water layer (*b*) If a second extraction is made using another 10 ml of CCl_4, calculate the quantity of iodine left behind after the second extraction. Given that the distribution coefficient of iodine between CCl_4 and water is 85.

Ans. (*a*) 0.222 mg (*b*) 0.012 mg

17. Prepare a liquid-liquid phase diagram for the system of partially miscible liquids *A* and *B*, where the (weight per cent *B*) at various temperature are:

T,°C	0	10	20	30	40
(wt% B)$_1$	30	37	45	53	64
(wt% B)$_1$	94	90	87	84	80

(*a*) What is the critical solution temperature?

(*b*) If a mixture containing 0.0600 kg of *B* and 0.0400 kg of *A* was at 25°C, what is the composition of the two phases in equilibrium and how much of each phase is present?

Ans. (*a*) 46°C

(*b*) 0.0702 kg of the phase having composition 49 per cent *B* and 0.0298 kg of the phase having composition 86 per cent *B*.

18. Explain the following:

(*a*) Effect of particle size on solubility.

(*b*) Insolubility of naphthalene in water.

(*c*) Insolubility of glucose in benzene.

(*d*) Effect of rise in temperature on solubility of a substance.

19. What are the similarities and dissimilarities in steam distillation and vaccum distillation?

20. Comment on the following:

(*a*) Like dissolves like.

(*b*) An ionic solid dissolves in water when hydration energy is more than the lattice energy.

Chapter 13

COLLIGATIVE PROPERTIES OF SOLUTIONS

13.1. INTRODUCTION

It has been observed that any solution containing some non-volatile solute exhibits the four properties: namely, (*i*) Vapor pressure lowering of the solvent, (*ii*) Boiling point elevation of the solution, (*iii*) Freezing point depression of the solution; and (*iv*) Osmosis and osmotic pressure of the solution. These four properties are collectively known as the colligative properties of solution. A colligative property is that property which depends only upon the number of solute particles present in the solution and in no way depends upon the chemical nature of these particles. The solute present should not undergo any association or dissociation. If there is association of solute particles, the number of particles actually added will become less and correspondingly, the properties mentioned above will be lowered. Similarly, if the solute particles are dissociated as in the case of electrolytes, the number of particles become larger than the original number and the value of the colligative properties become higher. Therefore, for such solutions in which the solute particles undergo association, or dissociation, some modification is essential over the laws deduced for solutions in which the solute particles are not associated or dissociated. While discussing these properties, it will be assumed that the solutions are very dilute and are ideal *i.e.*, the interactions between the solute particles are negligibly small.

The study of these properties has proved very helpful in the determination of molecular weight of the dissolved substances which are non-volatile.

13.2. VAPOR PRESSURE LOWERING OF THE SOLVENT

Whenever some non-volatile solute is added to a liquid solvent, vapor pressure of the solvent is lowered. This can be easily explained with the help of Raoults' Law. Consider any solution containing some non-volatile solute and let X_1 and X_2 be the mole fractions of the solvent and the solute respectively. If P° is the vapor pressure of the pure solvent and P is the vapor pressure of the solvent above the solution, then according to Raoult's Law

$$P = P^\circ X_1 \qquad \ldots (13.1)$$

Since X_1 is a positive quantity and is smaller than unity, therefore, P the vapor pressure of the solvent above the solution is always less than P°—the vapor pressure of the pure solvent. Hence, it can be said that *whenever a non-volatile solute is added to a solvent, the effect is the lowering of the vapor pressure of the solvent.*

The decrease in vapor pressure, $\triangle P$, is given by

$$\triangle P = P^\circ - P$$

Since from equation (13.1), $P = P^\circ X_1$

Therefore,
$$\triangle P = P^\circ - P^\circ X_1 \qquad \ldots (13.2)$$
$$= P^\circ(1 - X_1)$$

But
$$X_1 + X_2 = 1 \text{ or } 1 - X_1 = X_2$$

Hence equation (13.2) becomes

$$\triangle P = P^\circ X_2 \qquad \ldots (13.3)$$

This equation can also be written as

$$\frac{\triangle P}{P^\circ} = \frac{P^\circ - P}{P^\circ} = X_2 \qquad \ldots (13.4)$$

The quantity $\frac{P^\circ - P}{P^\circ}$ is known as the relative lowering of vapor pressure. It can readily be seen from equation (13.4) that the relative lowering of vapor pressure is a colligative property as it depends only on the mole fraction of the solute.

Equation (13.4) can be utilised to calculate the molecular weight of the solute if the vapor pressures of the pure solvent and the solution are known as follows:

Since the mole fraction of the solute, $X_2 = \frac{n_2}{n_1 + n_2}$

where n_2 is the number of moles of solute and n_1 is the number of moles of solvent, n_2 and n_1 are given by

$$n_2 = \frac{W_2}{M_2} \qquad \text{and} \qquad n_1 = \frac{W_1}{M_1}$$

W_2 is the weight of the solute of molecular weight M_2 and W_1 is the weight of the solvent of molecular weight M_1.

Therefore, equation (13·4) becomes

$$\frac{P^\circ - P}{P^\circ} = \frac{n_2}{n_1 + n_2} = \frac{W_2/M_2}{W_1/M_1 + W_2/M_2} \qquad \ldots (13.5)$$

Since the solution under consideration is very dilute, $n_2 << n_1$ and $n_1 + n_2 \approx n_1$

Thus
$$\frac{P^\circ - P}{P^\circ} = \frac{W_2 M_1}{W_1 M_2}$$

or
$$M_2 = \left(\frac{P^\circ}{P^\circ - P}\right)\left(\frac{W_2}{W_1}\right) M_1 \qquad \ldots (13.6)$$

If all the quantities on the right hand side are known, M_2 the molecular weight of the solute can be easily calculated.

Thermodynamic Deduction of Raoult's Law

The relation

$$\frac{P^\circ - P}{P^\circ} = X_2$$

can be deduced thermodynamically as follows :

The chemical potential of the solvent in the liquid phase of the system is given by

$$\mu(\text{liq}) = \mu^\circ(\text{liq}) + RT\ ln\ X_1$$

or
$$= \mu^\circ(\text{liq}) + RT\ ln\ (1 - X_2) \qquad \ldots (13.7)$$

and the chemical potential of the solvent in the vapor phase above the solution is given by

$$\mu\ (\text{vap}) = \mu^\circ\ (\text{vap}) + RT\ ln\ P \qquad \ldots (13.8)$$

At equilibrium, the chemical potential of the solvent in the vapor and liquid phase must be equal *i.e.*,

$$\mu\ (\text{vap}) = \mu\ (\text{liq})$$

or
$$\mu^\circ(\text{vap}) + RT\ ln\ P = \mu^\circ\ (\text{liq}) + RT\ ln\ (1 - X_2) \qquad \ldots (13.9)$$

when $X_2 = 0$, $P = P^\circ$ so that

$$\mu^\circ\ (\text{vap}) + RT\ ln\ P^\circ = \mu^\circ\ (\text{liq}) \qquad \ldots (13.10)$$

Subtracing equation (13.10) from equation (13.9), we have

$$RT\ ln\ P - RT\ ln\ P^\circ = RT\ ln\ (1 - X_2)$$

or
$$ln\ P/P^\circ = ln\ (1 - X_2)$$

or
$$\frac{P}{P^\circ} = 1 - X_2$$

Substracting both sides from unity, we get

$$1 - \frac{P}{P^\circ} = 1 - (1 - X_2)$$

or
$$\frac{P^\circ - P}{P^\circ} = X_2$$

Problem 13.1. When 18.04 g of the sugar alcohol mannitol were dissolved in 100 g of water, the vapor pressure of the later at 20°C was lowered from 17.535 mm to 17.226 mm of mercury. Calculate the molecular weight of mannitol.

Solution. In this case, W_1 is 100 g and M_1, the molecular weight of water is 18.02; W_2 is 18.04 g. The values of P^0 and P are 17.535 and 17.226 mm respectively. The relative lowering of the vapor pressure is obviously independent of the units used for the vapor pressures, provided P^0 and P are expressed in the same units. Hence by equation (13.5)

$$\frac{P^0 - P}{P^0} = \frac{W_2/M_2}{W_1/M_1 + W_2/M_2}$$

$$\frac{17.535 - 17.226}{17{\cdot}535} = \frac{18.04/M_2}{(100/18.02) + (18.04/M_2)}$$

or
$$M_2 = 181$$

Measurement of vapor pressure lowering. Since the value of vapor pressure lowering is very small, it is not convenient to measure the vapor pressure of the solvent and the solution separately by the methods described under vapor pressure in Chapter 4 and subtracting the two values. The lowering of vapor pressure of the solvent can be accurately determined by either of the two methods: (*i*) Static method, and (*ii*) Dynamic method.

In the static method, the vapor pressure of the solvent is determined in the usual manner by the barometric technique and then the lowering of vapor pressure is measured directly with the help of a differential manometer. One arm of the manometer is connected to the solution and the other to the pure solvent. Some non-volatile liquid of low density is used as the manometer indicator and the difference in vapor pressure is determined directly from the difference in level of the liquid in the two arms.

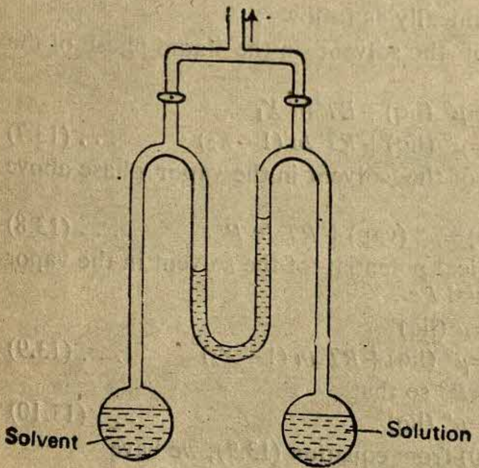
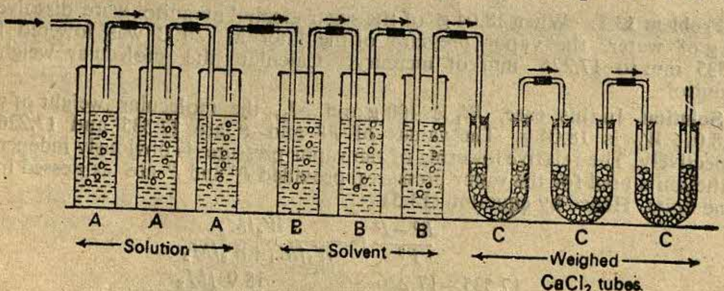


Fig. 13.1. Differential Manometer.

In the dynamic method, the gas saturation (or transpiration) method is generally employed. In this method, a steam of same volume of dry gas, say air, is passed through (*i*) the solution, (*ii*) the solvent, and (*iii*) suitable absorber to absorb the vapor of the solvent. Generally, anhydrous calcium chloride is used as an absorbing agent.

From the losses in weight of the solution and solvent and gain in the weight of the calcium chloride tube, the relative lowering can be calculated without actually determining the vapor pressure of the



Air saturated to P_s P° Increase in weight ∝ P°
Loss of weight ∝ P_s $P^\circ - P_s$

Fig. 13.2. Ostwald and Walker's apparatus.

solvent and solution separately. The apparatus required is shown in Fig. 13.2.

The solution is placed in three wash bottles *A* and pure solvent is placed in other three wash bottles *B*. They are followed by calcium chloride tubes. Air is then bubbled gradually to ensure that it gets saturated with the vapor in the bulb.

The weights of wash bottles containing the solvent and calcium chloride tubes are determined before and after the experiment.

The difference in weight of the solvent bottle $\propto P^\circ - P_s$ and the difference in weight of the calcium chloride tubes $\propto P^\circ$.

$$\text{Therefore, } \frac{\text{Loss in weight of solvent}}{\text{Gain in weight of CaCl}_2\text{ tubes}} = \frac{P^\circ - P_s}{P^\circ}$$

13.3. BOILING POINT ELEVATION OF SOLUTIONS

Boiling point of a liquid is defined as the temperature at which the vapor pressure of the liquid becomes equal to the confining pressure. It has been found that whenever some non-volatile solute is added to a liquid, its boiling point becomes higher. The difference between the boiling point of the solution and the boiling point of the pure solvent at any constant pressure is known as the boiling point elevation of the solution. Boiling point elevation is a direct consequence of vapor pressure lowering of the solvent by a non-volatile solute and can be readily explained in terms of it. Consider the "vapor pressure—temperature" curves for the pure solvent and solution as shown in Fig. 13.3.

In the diagram, curve *AB* represents the variation of vapor pressure of pure solvent with temperature. Similarly, curves *CD* and *EF* represent the variation of vapor pressure of two solutions of different concentrations with temperature (Solution II is more concentrated than solution I). The curves *CD* and *EF* must be below *AB* at all temperatures because the vapor presssure of solution is always lower than the solvent. Theboiling points of pure solvent, solution I and solution II at the same external pressure (1 atmosphere) are T_0, T_1 and T_2 respectively.

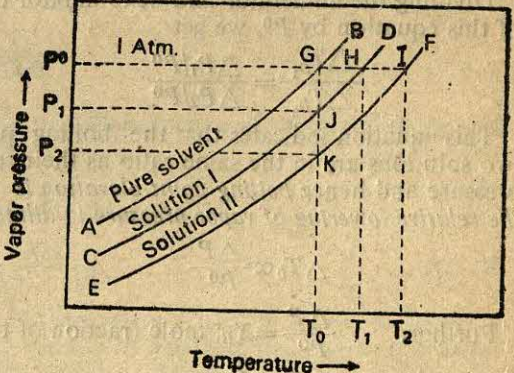


Fig. 13.3. Vapor pressure curves for solvent and solution.

It is evident from the diagram that the elevation of boiling point of solution I, $\triangle T_{b_1}=T_1-T_0$ is represented by distance GH and that of solution II, $\triangle T_{b_2}=T_2-T_0$ is represented by GI.

Points G, J and K represent the vapor pressure of pure solvent, solution I and solution II, respectively at the same temperature, T_0. The vapor pressures corresponding to these points are P°, P_1 and P_2 respectively. The distances GJ and GK represent the lowering of vapor pressure of solution I and solution II and are given by (P^0-P_1) and (P^0-P_2) respectively.

Since the solutions are dilute, their vapor pressure curves are nearly parallel to the vapor pressure curve for pure solvent; particularly in the region of boiling point and to a good approximation may be considered to be straight lines.

Triangles GHJ and GIK are similar.

From analytical geometry,

$$\frac{GH}{GI}=\frac{GJ}{GK}$$

$GH=\triangle T_{b_1}$ for solution $\text{I}=T_1-T_0$

$GI=\triangle T_{b_2}$ for solution $\text{II}=T_2-T_0$

$GJ=\triangle P_1$ for solution $\text{I}=P^0-P_1$

$GK=\triangle P_2$ for solution $\text{II}=P^0-P_2$

Therefore

$$\frac{T_1-T_0}{T_2-T_0}=\frac{P^0-P_1}{P^0-P_2}$$

or

$$\frac{\triangle T_{b_1}}{\triangle T_{b_2}}=\frac{\triangle P_1}{\triangle P_2}$$

Dividing the numerator and denominator of the right hand side of this equation by P^0, we get

$$\frac{\triangle T_{b_1}}{\triangle T_{b_2}}=\frac{\triangle P_1/P^0}{\triangle P_2/P^0}$$

This equation indicates that the boiling point elevations for the two solutions are in the same ratio as their relative lowering of vapor pressure and hence *boiling point elevation is directly proportional to the relative lowering of vapor pressure in dilute solution, i.e.,*

$$\triangle T_b \propto \frac{\triangle P}{P^0}$$

Further, $\frac{\triangle P}{P^0}=X_B$; mole fraction of the solute

Therefore, $\triangle T_b \propto X_B$

or $\triangle T_b=AX_B$

where A is a constant of proportionality.

Again $X_B=\frac{n_B}{n_A+n_B}\approx\frac{n_B}{n_A}$ (since the solutions are very dilute) where n_B is the number of moles of solute and n_A is the number of moles of solvent

and
$$\frac{n_B}{n_A}=\frac{W_B/M_B}{W_A/M_A}$$

where the terms W and M represent the weights and molecular weights of the respective constituents.

Hence
$$\triangle T_b=A\,\frac{W_BM_A}{W_AM_B}$$
$$=AM_A.\;\frac{W_B}{M_B}\cdot\frac{1}{W_A}$$

Since M_A is constant for a particular solvent, both constants A and M_A are amalgamated into a single constant, k_b.

Thus
$$\triangle T_b=k_b\,\frac{W_B}{M_B}\cdot\frac{1}{W_A} \qquad \ldots (13.11)$$

The constant k_b is known as the *ebullioscopic constant* or *boiling point elevation constant* for a solvent and signifies the boiling point elevation for one molal solution of a solute in a solvent, *i.e.*,

$\triangle T_b=k_b$ if $\quad \frac{W_B}{M_B}\,(=n_B)=1$ and $W_A=1$ gram.

If one mole of the solute is dissolved in 1000 grams of the solvent, the constant is known as the *molal elevation constant* and is defined as the elevation in boiling point obtained on dissolving one mole of a non-volatile solute in 1000 grams of the solvent. In terms of molality, equation (13.11) can be written as

$$\triangle T_b=K_b.\;\frac{W_B}{M_B}\cdot\frac{1}{W_A}\times 1000 \qquad \ldots (13.12)$$

where
$$K_b=\frac{k_b}{1000}$$

The quantity $\frac{W_B}{M_B}\cdot\frac{1}{W_A}\times 1000$ is known as the molality (m) of the solution.

Thermodynamically, it can be showed that

$$K_b=\frac{RT_0^2}{\triangle h_v\times 100} \qquad \ldots (13.13)$$

where R is the usual gas constant and is equal to 1.987 calories, T_0 is the boiling point of pure solvent on absolute scale and $\triangle h_v$ is the heat of vaporisation per gram of the solvent.

Thermodynamic method. Equation (13.11) can also be deduced thermodynamically. This derivation will give the value of the constant K_b, in terms of the properties of the solvent.

Consider the curves AB and CD in Fig. 13.3. Since points J

and H represent the vapor pressure of solution corresponding to temperatures T_0 and T_1 respectively, then from Clausius-Clapeyron equation,

$$ln \frac{P^0}{P_1}=\frac{\triangle H_v}{R}\left(\frac{T_1-T_0}{T_1T_0}\right) \qquad \ldots (13.14)$$

where P^0 is the vapor pressure of the solution at temperature T_1 and P_1 is the vapor pressure of the solution at temperature T_0. R is constant and its value in calories is 1.987. $\triangle H_v$ is the heat of vaporisation per mole of the solvent from the solution. But since the solution is dilute, it can be taken as heat of vaporisation per mole of the solvent. Moreover, for dilute solution, T_1 is not very different from T_0 and $T_1\,T_0$ may be written as T_0^2. (T_1-T_0) is the boiling point elevation and is equal to $\triangle T_b$.

Therefore, equation (13.14) becomes

$$ln \frac{P^0}{P_1}=-ln \frac{P_1}{P^0}=\frac{\triangle H_v}{R}\ \frac{\triangle T_b}{T_0^2} \qquad \ldots (13.15)$$

In equation (13.15), P_1 is the vapor pressure of solution at temperature T_0 and P^0 is the vapor pressure of the pure solvent at the same temperature. If X_A is the mole fraction of the solvent and X_B is the mole fraction of the solute in the solution, then from Raoult's Law,

$$P_1=P^0X_A=P^0(1-X_B)$$

or

$$\frac{P_1}{P^0}=(1-X_B) \qquad \ldots (13.16)$$

Substituting this value in equation (13.15),

$$-ln\ (1-X_B)=\frac{\triangle H_v}{R}\cdot\frac{\triangle T_b}{T_0^2} \qquad \ldots (13.17)$$

Now,

$$ln\,(1-X_B)=-X_B-\frac{X_B^2}{2}\ \frac{-X_B^3}{3}\ldots$$

Since X_B is small for dilute solution,

$$ln\,(1-X_B)\approx -X_B$$

Therefore, equation (13.17) becomes

$$X_B=\frac{\triangle H_v}{R}\cdot\frac{\triangle T_b}{T_0^2}$$

or

$$\triangle T_b=\frac{RT_0^2}{\triangle H_v}\cdot X_B \qquad \ldots (13.18)$$

This result can also be obtained by applying *chemical potential concept* as shown below:

Since at equilibrium, the chemical potential of the solvent in the solution (liquid phase) is equal to the chemical potential of the solvent in the vapor phase, we have

$$\mu_{liq}\,(T, P, X_A)=\mu_{vap}\,(T, P)$$

But, since the solution is ideal, $\mu_{liq}(T, P, X_1)$ is given by

$$\mu_{liq}(T, P, X_A) = \mu^\circ_{liq}(T, P) + RT \ln X_A$$

Hence, $\mu^\circ_{liq}(T, P) + RT \ln X_A = \mu_{vap}(T, P)$

or $$\ln X_A = \frac{\mu_{vap}(T, P) - \mu^\circ_{liq}(T, P)}{RT}$$

The molar free energy of vaporisation is

$$\triangle G_{vap} = \mu_{vap}(T, P) - \mu^\circ_{liq}(T, P)$$

so that $\ln \ X_A = \frac{\triangle G_{vap}}{RT}$

Differentiating this equation with respect to X_A, keeping the pressure constant, we get

$$\frac{1}{X_A} = \frac{1}{R}\left[\frac{\partial\left(\frac{\triangle G_{vap}}{T}\right)}{\partial T}\right]_P \left(\frac{\partial T}{\partial X_A}\right)_P$$

Using the Gibbs-Helmholtz relationship (9.50), this takes the form

$$\frac{1}{X_A} = -\frac{\triangle H_v}{RT^2}\left(\frac{\partial T}{\partial X_A}\right)_P$$

which on integration yields

$$\int_1^{X_A} \frac{dX_A}{X_A} = -\frac{1}{R}\int_{T_0}^{T_1} \frac{\triangle H_v}{T^2} dT$$

where the lower limit corresponds to pure solvent with a boiling point T_0 and the upper limit corresponds to a solution with boiling point T_1. The integration is done on the assumption that $\triangle H_v$ is independent of temperature:

$$\ln X_A = -\frac{\triangle H_v}{R}\left(-\frac{1}{T_1} + \frac{1}{T_0}\right)$$

$$= -\frac{\triangle H_v}{R}\left(\frac{T_1 - T_0}{T_0 T_1}\right)$$

But $T_1 - T_0 = \triangle T_b$ and $T_0 T_1 \approx T_0^2$

Therefore, $\ln \ X_A = -\frac{\triangle H_v}{RT_0^2} \cdot \triangle T_b$

For a very dilute solution, $\ln \ X_A = \ln(1 - X_B) \approx -X_B$

Hence, $$-X_B = -\frac{\triangle H_v}{RT_0^2} \triangle T_b$$

or $$\triangle T_b = \frac{RT_0^2}{\triangle H_v} \cdot X_B$$

Again $$X_B=\frac{n_B}{n_A+n_B}\approx\frac{n_B}{n_A}=\frac{W_B}{M_B}\cdot\frac{M_A}{W_A}$$

$$\therefore \quad \triangle T_b=\frac{RT_0^2}{\triangle H_v}\cdot\frac{W_BM_A}{W_AM_B}$$

or $$\triangle T_b=\frac{RT_0^2}{\triangle h_v}\cdot\frac{W_B}{M_B.W_A} \qquad \ldots (13.19)$$

where $\triangle h_v$ is equal to $\frac{\triangle H_v}{M_A}$ and is the heat of vaporisation per gram of the solvent.

The common practice in boiling point elevation is to express the concentration in terms of molality *i.e.*, the number of moles of solute per 1000 grams of the solvent. In the solution under consideration, $\frac{W_B}{M_B}$ is the number of moles of solute dissolved in W_A grams of the solvent.

Molality (m) is given by

$$m=\frac{W_B}{M_B}\cdot\frac{1}{W_A}\times 1000$$

or $$\frac{W_B}{M_B}\cdot\frac{1}{W_A}=\frac{m}{1000} \qquad \ldots (13.20)$$

Substituting this value in equation (13.19)

$$\triangle T_b=\left(\frac{RT_0^2}{1000\triangle h_v}\right)m \qquad \ldots (13.21)$$

For any given solvent, all the quantities in the bracket are constant and, therefore, the whole term being a constant is replaced by another constant, K_b.

Therefore, $\triangle T_b=K_b.m$ ... (13.22)

where $$K_b=\frac{RT_0^2}{1000\triangle h_v} \qquad \ldots (13.23)$$

Boiling point elevation is a colligative property can be said from equation (13.22) according to which boiling point elevation of a solution is directly proportional to the molality of the solute provided the solution is dilute and obeys Raoult's Law.

Calculation of molecular weight of the solute from boiling point elevation. As shown earlier,

$$\triangle T_b=K_b.\frac{W_B}{M_B}\cdot\frac{1000}{W_A}$$

or $$M_B = K_b . \frac{1000\, W_B}{\triangle T_b . W_A} \qquad \ldots (13.24)$$

This equation permits the calculation of molecular weight of the solute from a knowledge of weights of the solute and solvent, boiling point elevation and constant K_b.

The value of constant K_b can be determined from the equation

$$K_b = \frac{RT_0^2}{1000 \triangle h_v}$$

Problem 13.2. A 2% solution (by weight) of a substance of unknown molecular weight in toluene as a solvent has a vapor pressure of 752.4 mm Hg at 110°C and a normal boiling point of 110.25°C. The normal boiling point of toluene is 110.00°C and the solute is non-volatile. Calculate the molecular weight of the solute and the heat of vaporisation (per gram) of toluene ($C_6H_5CH_3$).

Solution. The vapor pressure lowering at 110°C is

$$760 - 752.4 \text{ or } 7.6 \text{ mm Hg.}$$

Therefore, from Raoult's Law of vapor pressure lowering,

$$X_B = \frac{7.6}{760} = 0.01$$

Taking 100 grams of solution as a basis, there are 2.0 grams of solute and 98 grams or $\left(\frac{98}{92}\right) = 1.065$ mol of toluene.

Therefore $$0.01 = \frac{n_B}{n_B + 1.065}$$

or $$n_B = 0.0106$$

and the molecular weight of the substance

$$= \frac{2}{0.0106} = 189$$

Again, the molality (m) of the solution is

$$= 0.01 \times 10{,}9 = 0.109$$

$$\triangle T_b = 110.25 - 110 = 0.25°\text{C}$$

and $$T^0 = 273 + 110 = 383.0 \text{ K.}$$

Therefore, $$\triangle T_b = \frac{RT_0^2\, m}{1000 \triangle hv}$$

or $$\triangle h_v = \frac{RT_0^2\, m}{1000 \triangle T_b} = \frac{1.987 \times (383)^2 \times 0.109}{1000 \times 0.25}$$

$$= 127 \text{ cal/g}$$

Therefore, heat of vaporisation

$$\triangle h_v = 127 \text{ cal/g}$$

Experimental determination of boiling point elevation. While determining boiling point of a solution, care is taken to avoid superheating. There are two main methods generally employed for the determination of boiling point elevation:

(*i*) **The landsberger method**. In this method, the solution is heated to the boiling point by passing into it the vapors of pure solvent. When vapors condense, latent heat is given up and this latent heat of condensation raises the temperature of solution to boiling point. Heating through vapors is done to avoid the danger of superheating.

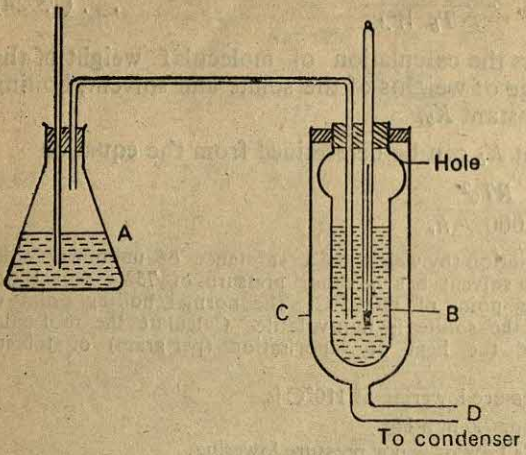


Fig. 13.4. Landsberger's apparatus.

The apparatus consists of a flask *A*, containing the pure solvent and is connected through a delivery tube to a tube *B* graduated in c.c's. Towards the top of this tube, there is a hole which permits communication with the outer vessel *C*. *A* condenser to condense the escaping vapors is attached to *D*. The tube *B* is also fitted with a thermometer.

To start with, a known quantity of the pure solvent is taken into *B*; the thermometer is lowered in the solvent and a stream of vapors of the solvent from *A* is passed into it until the liquid begins to boil. When the temperature indicated by the thermometer becomes constant, it is noted. This gives the boiling point of the pure solvent. A weighed quantity of the solute under investigation is then put into the tube *B* and the passage of vapors continued until the temperature is constant. This gives the boiling point of the solution. The volume of the solution in tube *B* is noted. If the density of the solvent is known, the mass of the solvent present in the solution can be easily found. It is assumed that the solute does not occupy any volume.

The difference in the two readings gives the boiling point elevation of the solution.

(*ii*) **Cottrell's method.** In this method, a known quantity of the solvent is taken in the boiling tube *A*, which is graduated. An inverted funnel tube is placed in the boiling tube. The bubbles formed at the pieces of porous pot in the liquid force through this funnel a stream of boiling liquid and vapor over the bulb of the thermometer *E* which is placed above the surface of the liquid. The bulb is thus covered with a thin layer of boiling liquid in equilibrium with its vapors. This ensures that the temperature recorded by the thermometer is the true boiling point of the liquid. The care is taken to prevent the cold condensate from reaching

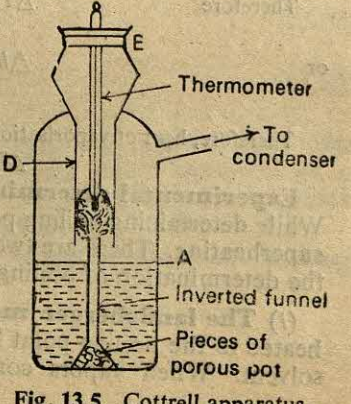


Fig. 13.5. Cottrell apparatus.

the thermometer. This is due with the help of sheath D.

A weighed quantity of the solute is then added to the solvent and the boiling point of the solution is determined. Difference in the two readings gives the boiling point elevation of the solution. The volume of the solution is noted and knowing the density of the solvent, mass of the solvent can be easily determined.

13.4. FREEZINE POINT DEPRESSION OF SOLUTIONS

On cooling a dilute solution, a temperarure is ultimately reached at which solid solvent begins to separate from the solution. This temperature at which the precipitation of the solid solvent begins is the *freezing point* of the solution. At this temperature, solid solvent and solution are in equilibrium and consequently they must have the same vapor pressures.

It is observed that freezing point of a solution is lower than that of pure solvent. This is again a direct consequence of the lowering of the vapor pressure of the pure solvent by the dissolved solute. Consider the vapor pressure—temperature diagram as shown in Fig 13.6.

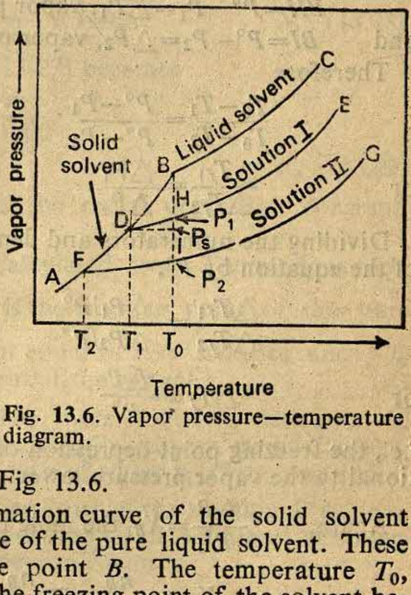


Fig. 13.6. Vapor pressure—temperature diagram.

In the diagram, AB is the sublimation curve of the solid solvent and BC is the vapor pressure curve of the pure liquid solvent. These two curves are intersecting at the point B. The temperature T_0, corresponding to this point, is the freezing point of the solvent because at this temperature, the solid and the liquid phases are in equilibrium with each other and have identical vapor pressures. DE and FG are the vapor pressure curves of solutions I and II (concentration of solution II is greater than the concentration of solution I). These two curves are intersecting the sublimation curve at points D (temperature T_1) and F (temperature T_2) respectively. Therefore, T_1 and T_2 are the freezing points of solution I and solution II respectively. Both T_1 and T_2 are lower than T_0.

The freezing point depression of solution I is

$$\Delta T_{f1}=T_0-T_1$$

and the freezing point depression of solution II is

$$\Delta T_{f2}=T_0-T_2$$

Let P° is the vapor pressure of solid and the pure liquid solvent at temperature T_0 and P_1 and P_2 are the vapor pressures of solutions I and II respectively at the same temperature. For dilute solutions, the freezing point depression will be small and to a good approximation, the vapor pressure curves may be considered to be parallel straight lines in the vicinity of the freezing point.

Since the two triangles BHD and BIF are similar, therefore,

$$\frac{DH}{FI}=\frac{BH}{BI}$$

But $DH=T_0-T_1=\triangle T_{f1}$, the freezing point depression for solution I

$FI=T_0-T_2=\triangle T_{f2}$, the freezing point depression for solution II

$BH=P^\circ-P_1=\triangle P_1$, vapor pressure lowering for solution I

and $BI=P^\circ-P_2=\triangle P_2$, vapor pressure lowering for solution II

Therefore

$$\frac{T_0-T_1}{T_0-T_2}=\frac{P^\circ-P_1}{P^\circ-P_2}$$

or

$$\frac{\triangle T_{f1}}{\triangle T_{f2}}=\frac{\triangle P_1}{\triangle P_2}$$

Dividing the numerators and denominator of the right hand side of the equation by P°,

$$\frac{\triangle T_{f1}}{\triangle T_{f2}}=\frac{\triangle P_1/P^\circ}{\triangle P_2/P^\circ}$$

or

$$\triangle T_f \propto \frac{\triangle P}{P^\circ} \qquad \ldots (13.25)$$

i.e., the freezing point depression of a solution is directly proportional to the vapor pressure lowering of the solvent.

Again, $\frac{\triangle P}{P^\circ}=X_B$, the mole fraction of the solute and

$$X_B=\frac{n_B}{n_A+n_B}\approx\frac{n_B}{n_A}=\frac{W_B}{M_B}\times\frac{M_A}{W_A}\,.$$

All the symbols have got the same meanings as given under boiling point elevation.

Therefore, equation (13.25) becomes

$$\triangle T_f \propto \frac{W_B M_A}{W_A M_B}$$

or

$$\triangle T_f=A\frac{W_B M_A}{W_A M_B} \qquad \ldots (13.26)$$

where A is some proportionality constant. Again, for a given solvent, M_A is constant. Therefore, both the constants A and M_A are replaced by another constant k_f in the equation (13.26).

Hence

$$\triangle T_f=k_f\,\frac{W_B}{W_A M_B} \qquad \ldots (13.27)$$

The constant k_f is known as the *depression constant* or *cryoscopic constant* and depends on the nature of the solvent. If 1 mole of the solute $\left(i.e., \frac{W_B}{M_B}=1 \right)$ is dissolved in 1 gram of the solvent ($W_A=1$ gram), then from equation (13.27), $\triangle T_f=k_f$ *i.e.*, the depression constant becomes freezing point depression when 1 mole of any solute is dissolved in 1 gram of the solvent.

But generally in dilute solutions, concentration is expressed in terms of molatity m, which is defined as the number of moles of solute dissolved per 1000 grams of the solvent. For the solution under consideration

$$m=\frac{W_B}{W_A M_B}\times 1000 \qquad \ldots (13.28)$$

In terms of molality, equation (13.27) becomes

$$\triangle T_f=k_f.\ \frac{m}{1000}$$

or

$$\triangle T_f=K_f.m \qquad \ldots (13.29)$$

where $K_f\ (=k_f/1000)$ is known as the molal depression constant. For a molal solution, $\triangle T_f=K_f$.

The numerical value of K_f, as calculated from Thermodynamics, is given by $\frac{RT_{02}}{1000\ \triangle h_f}$, where T_0 is the freezing point of the pure solvent, R is the usual gas constant equal to 1.987 calories and $\triangle h_f$ is the latent heat of fusion per gram of the solvent.

Thermodynamic method. The more complete derivation of equation (13.29) is done thermodynamically making use of Clausius-Clapeyron equation and Raoult's Law of vapor pressure lowering.

In the diagram, P_1 is the vapor pressure of the solution I at temperature T_0 and P_s is the vapor pressure of the solution I at temperature T_1. Applying Clausius-Clapeyron equation

$$ln\ \frac{P_s}{P_1}=\frac{\triangle H_v}{R}\left(\frac{T_1-T_0}{T_1 T_0}\right) \qquad \ldots (13.30)$$

where $\triangle H_v$ is the molar heat of vaporisation of the solvent.

Again, for the solid, P° is the vapor pressure at temperature T_0 and P_s is the vapor pressure at temperature T_1. Therefore,

$$ln\ \frac{P_s}{P^\circ}=\frac{\triangle H_s}{R}\left(\frac{T_1-T_0}{T_1 T_0}\right) \qquad \ldots (13.31$$

where $\triangle H_s$ is the molar heat of sublimation of the solid solvent.

Subtracting equation (13.30) from equation (13.31)

$$ln\ P_s - ln\ P^\circ - ln\ P_s + ln\ P_1$$

$$=\frac{\triangle H_v}{R}\left(\frac{T_0-T_1}{T_0 T_1}\right)-\frac{\triangle H_s\,(T_0-T_1)}{RT_0 T_1}$$

$$ln\, P_1 - ln\, P^\circ = -\frac{(\triangle H_s - \triangle H_v)(T_0 - T_1)}{RT_0T_1}$$

or $$ln\, \frac{P_1}{P^\circ} = -\frac{\triangle H_f}{R}\, \frac{\triangle T_{f1}}{T_0T_1} \quad \ldots (13.32)$$

where $\triangle H_f = \triangle H_s - \triangle H_v$ is the molar heat of fusion of the solvent and

$\triangle T_f = T_0 - T_1$ is the freezing point depression of the solution.

Since the solution is dilute, $T_0T_1 \approx T_0^2$. Again P° is the vapor pressure of the solvent at temperature T_0 and P_1 is the vapor pressure of the solution 1 at the same temperature. Therefore, from Raoult's Law

$$\frac{P_1}{P^\circ} = X_A = (1 - X_B)$$

where X_A and X_B are the mole fractions of the solvent and the solute respectively in the solution.

Therefore, equation (13.32) becomes

$$ln(1 - X_B) = -\frac{\triangle H_f}{R}.\, \frac{\triangle T_f}{T_0^2} \quad \ldots (13.33)$$

But $ln\,(1 - X_B) \approx -X_B$ (when X_B is very small)

Therefore $$-X_B = -\frac{\triangle H_f}{R}.\, \frac{\triangle T_f}{T_0^2}$$

or $$\triangle T_f = \frac{RT_0^2}{\triangle H_f}.\, X_B \quad \ldots (13.34)$$

This result can also be obtained by applying *chemical potential concept* as follows:

At equilibrium, the chemical potential of the solvent in both the liquid and solid phases will be same *i.e.*,

$$\mu_{\text{liq}}(T, P, X_A) = \mu_{\text{solid}}(T, P)$$

But, for dilute solutions, $\mu_{\text{liq}}(T, P, X_A)$ is given by

$$\mu_{\text{liq}}(T, P, X_A) = \mu^\circ_{\text{liq}}(T, P) + RT\, ln\, X_A$$

Hence $$\mu^\circ_{\text{liq}}(T, P) + RT\, ln\, X_A = \mu_{\text{solid}}(T, P)$$

or $$ln\, X_A = \frac{\mu_{\text{solid}}(T,P) - \mu^\circ_{\text{liq}}(T, P)}{RT}$$

The molar free energy of fusion of the pure solvent is

$$\triangle G_{\text{fus}} = \mu^\circ_{\text{liq}}(T, P) - \mu_{\text{solid}}(T, P)$$

so that $$ln\, X_A = -\frac{\triangle G_{\text{fus}}}{RT}.$$

Differentiating this equation with respect to T at constant P, we obtain

$$\left(\frac{\partial \ln X_A}{\partial T}\right)_P = -\frac{1}{R}\left[\frac{\partial\left(\frac{\triangle G_{\text{fus}}}{T}\right)}{\partial T}\right]_P \left(\frac{\partial T}{\partial X_A}\right)_P$$

Using the Gibbs-Helmholtz relation, this reduces to

$$\left(\frac{\partial \ln X_A}{\partial T}\right)_P = \frac{\triangle H_f}{RT^2}\left(\frac{\partial T}{\partial X_A}\right)_P$$

which on integration yields

$$\int_{l}^{X_A} \frac{dX_A}{X_A} = \frac{1}{R}\int_{T_0}^{T_1} \frac{\triangle H_f}{T^2}\, dT$$

where the lower limit $X_A=1$ corresponds to pure solvent having a freezing points T_0 and the upper limit X_A corresponds to a solution having the freezing point T_1. The integration is done on the assumption that $\triangle H_f$ is independent of temperature:

$$\ln X_A = \frac{\triangle H_f}{R}\left(-\frac{1}{T_1}+\frac{1}{T_0}\right)$$

$$= -\frac{\triangle H_f}{R}\left(\frac{T_0-T_1}{T_1 T_0}\right)$$

But $\qquad T_0-T_1=\triangle T_f$ and $T_1T_0 \approx T_0^2$

With these substitution, we obtain

$$\ln X_A = -\frac{\triangle H_f}{RT_0^2}\cdot \triangle T_f$$

For a very dilute solution,

$$\ln X_A = \ln\,(1-X_B) \approx -X_B$$

Thorefore, $\qquad -X_B = -\frac{\triangle H_f}{RT_0^2}\cdot \triangle T_f$

or $\qquad \triangle T_f = \frac{RT_0^2}{\triangle H_f}\cdot X_A.$

But $\qquad X_B \approx \frac{n_B}{n_A} = \frac{W_B M_A}{W_A M_B}$

Hence $\qquad \triangle T_f = \frac{RT_0^2}{\triangle H_f}\cdot \frac{W_B\, M_A}{W_A\, M_B}$

or $\qquad = \frac{RT_0^2}{\triangle h_f}\;\frac{W_B}{W_A M_B} \qquad \ldots (13.35)$

where $\triangle h_f \left(=\frac{\triangle H_f}{M_A}\right)$ is the latent heat of fusion per gram of the solvent.

If the molality of the solution is designated by m, then

$$m = \frac{W_B}{W_A \, . \, M_B} \times 1000$$

In terms of molatity, equation (13.35) becomes

$$\triangle T_f = \left(\frac{RT_0^2}{1000 \, \triangle h_f} \right) m$$

$$= K_f \, . \, m \qquad \ldots (13.36)$$

where $$K_f = \frac{RT_0^2}{1000 \triangle h_f} \qquad \ldots (13.37)$$

Its physical significance has already been discussed.

Calculation of molecular weight from freezing point depression. This can be easily determined if K_f is known. The value of K_f can be readily calculated from the equation

$$K_f = \frac{RT_0^2}{1000 \, \triangle h_f}$$

Knowing K_f, molecular weight of the solute is then calculated from the equation

$$M_B = K_f \, \frac{1000 \, W_B}{\triangle T_f \, . \, W_A} \qquad \ldots (13.38)$$

Freezing point depression—a colligative property. Since $\triangle T_f \propto m$ and m depends on the number of moles of solute, therefore, freezing point depression is a colligative property.

Problem 13.3. For a solution of 0.911 gm of carbon tetrachloride dissolved in 50.00 gm of benzene, the freezing point depression was found to be 0.603°C. Calculate the molecular weight of the carbon tetrachloride. K_f given is 5.12.

Solution. According to equation,

$$M_B = K_f \, \frac{1000 \, W_B}{\triangle T_f \, W_A}, \text{ using } K_f = 5.12$$

we have

$$M_A = \frac{5.12 \times 1000 \times 1.911}{0.603 \times 50.00} = 155$$

Thus, the molecular weight of carbon tetrachloride is 155.

Experimental determination of freezing point depression

(*i*) *The Beckmann method.* Freezing point depression can be measured very accurately with this method. The apparatus is shown in Fig. 13.7. It consists of a freezing tube *A* containing the solvent whose freezing point is to be determined and is provided with a side tube *B* through which known weight of the solute can be introduced. This tube is fitted with a Backman. Thermometer and a stirrer and is surrounded by an air jacket. The function of air jacket is to prevent rapid cooling of the contents of the freezing tube. The whole assembly is placed in a larger outer vessel which contains the freezing mixture.

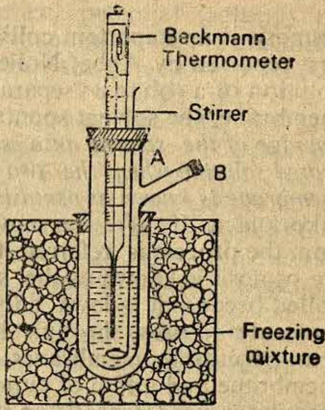


Fig. 13.7. Beckmann's freezing point apparatus.

The apparatus is set up and the freezing point of a known weight of the solvent is determined. The solvent is allowed to cool by about 0.5° below its freezing point. It is then stirred vigorously. During stirring, crystallisation starts and temperature rises. The rise in temperature continues till freezing point. At freezing point, the temperature remains constant and is recorded. A known weight of the solute under investigation is then introduced through the side tube, completely dissolved and the freezing point of the solution is determined. The difference in the two readings gives the freezing point depression for the solution of known composition.

(*ii*) *The Rast Camphor method.* This method makes use of the fact that molal depression constant of camphor is very high and is about 40 per 1000 grams. This means that when 1 mole of a solute is dissolved in 1000 grams of camphor, freezing point is lowered by about 40°C. The fall in temperature is so great that an ordinary thermometer can be employed for the determination of freezing point depression with sufficient accuracy.

The melting point of the pure camphor is first determined in the usual manner in a capillary tube. A known weight of the solute under investigation is mixed about ten times its weight with camphor and an intimate mixture is obtained be fusing them together. The mass is then cooled and powdered. The melting point of the mixture is then determined. This gives the freezing point of the solution.

The difference in the two readings gives the freezing point depression of the solution.

This method is applicable only for those substances which are soluble in camphor.

13.5. OSMOSIS AND OSMOTIC PRESSURE

Osmosis is an important colligative property of solution and was first reported by Abbe Nollet in 1748. He observed that when a solution of a solute is separated from pure solvent by a suitable membrane, the solvent spontaneously passed into the solution. *This passage of the solvent into solution or from more dilute to concentrated solution when the two are separated from each other by a membrane is known as osmosis.* In osmosis, only the flow of solvent takes place. If there is a movement of solute in the opposite direction, the process is referred to as diffusion. The membrane used for osmosis is known as the semi-permeable membrane. This is so called because it allows only solvent molecules and not the solute molecules to pass through it freely. There are various types of semi-permeable membranes such as animal membranes, cellulose membrane and a film of cupric ferrocyanide, $Cu_2[Fe(CN)_6]$ etc. The membrane used depends on the nature of the solvent and solute.

The phenomena of osmosis can readily be explained with the help of apparatus shown in Fig. 13.8. An inverted thistle funnel, the end of which is tied by an animal membrane, is partially filled with a concentrated solution of sugar. This is immersed into a beaker containing pure water. Due to osmosis, water will begin to pass through the membrane and the level of the sugar solution in the tube begins to rise until it reaches a definite height. depending on the concentration of the solution. The hydrostatic pressure, set up from the differences in levels of the sugar solution in the tube and the surface of the pure water is the *osmotic pressure* of the solution and is defined as *the mechanical pressure which must be applied on a solution to prevent the passage of solvent into the solution when the two are separated from each other by a semi-permeable membrane.*

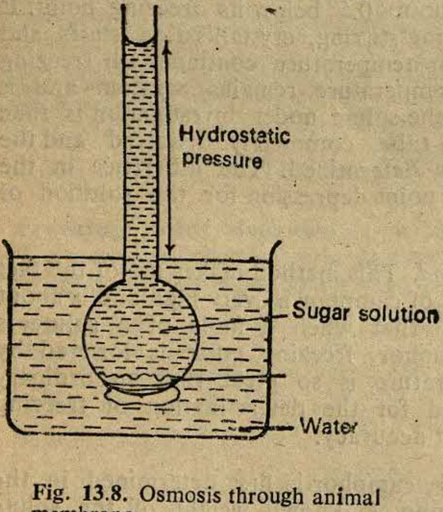


Fig. 13.8. Osmosis through animal membrane.

A better definition of the osmotic pressure of a solution is based on the chemical potential of the solvent. The chemical potential of a solvent in a dilute solution is given by

$$\mu_{1(\text{solution})} = \mu_1^\circ{}_{(\text{liq})} + RT \ln X_1$$

where $\mu_1^\circ{}_{(\text{liq})}$, is the chemical potential of the pure solvent and X_1 is the mole fraction of the solvent. Since X_1 is less than 1 and its logarithm is negative, it follows from the equation that $\mu_1^\circ{}_{(\text{solution})}$ is less than $\mu_1^\circ{}_{(\text{liq})}$. In order to establish equilibrium, there is flow of solvent from high chemical potential (solvent) to low chemical potential (solution) and flow continues till the chemical potentials are equal. Again, we know that the chemical potential can be increased by increasing the pressure. Therefore, if the pressure of the solution is increased, the chemical potential of the solution will increase till it becomes equal to chemical potential of the pure solvent. At this stage, there will be no flow of the solvent to the solution side. Hence, in terms of chemical potential, osmotic pressure of a solution is defined as the extra pressure applied to a solution so that the chemical potential of the solvent in the solution becomes equal to that of the pure solvent. Osmotic pressure depends on the nature of the solvent and the solute but is independent of the nature of the membrane as long as it is semi-permeable and is a measure of difference in pressure of the solvent and the solution.

The arrangement, shown in Fig. 13.8, cannot be satisfactorily employed to measure osmotic pressure quantitatively. Consider the diagram as shown in Fig. 13.9.

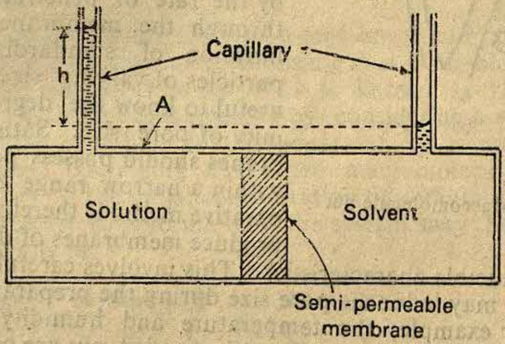


Fig. 13.9. Schematic diagram of the apparatus used to determine the osmotic pressure of a solution.

A is a chamber fitted at both ends with very thin bore capillary tubes. This chamber is divided by a semi-permeable membrane into two compartments of which the right one is filled with the solvent and the other with the solution. At the beginning of the experiment, levels of the liquid in the two capillaries are kept same. Due to osmosis, solvent begins to pass through the membrane into the solution. As a result of this, the level of the liquid in the capillary on the solution side begins to rise and the level on the solvent side starts descending until equilibrium is reached. The difference in capillary levels gives the osmotic pressure. Instead of using a capillary on the solution side, a piston can also be used so that pressure can be applied just to prevent osmosis. This pressure will then be equal to osmotic pressure.

13.6. DIALYSING MEMBRANES

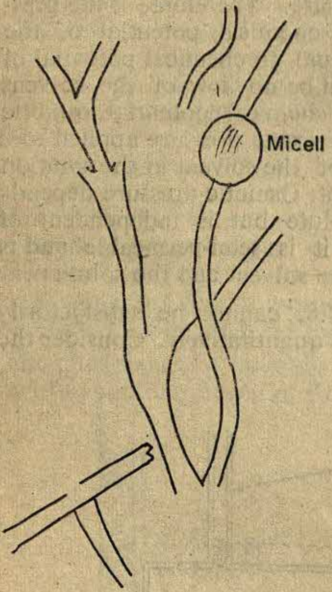


Fig. 13.10. Macromolecule net work.

The membranes that are used in dialysis and ultrafiltration are usually derivatives of cellulose (*e.g.*, cellulose acetate, nitrocellulose) and may be classed as xerogels. The structure of these materials may be regarded as microporous network of macromolecules as shown in Fig. 13.10 which shows that the molecules are usually aggregated into bundles or micelles by secondary forces such as hydrogen bonding.

Pore Size

This is important in determining the contribution of the sieve effect to the permeability of a membrane. The average pore size may be determined by the rate of penetration of water through the membrane, or by the filtration of standardised colloidal particles of varying sizes. It is also useful to know the degree of uniformity of pore size. Satisfactory membranes should possess pores that fall within a narrow range of sizes. Preparative methods therefore attempt to produce membranes of different grades with reproducible characteristics. This involves careful control of all factors that may influence pore size during the preparation of membranes. For example, the temperature and humidity under which evaporation of the volatile solvent is carried out are controlled since the final pore size depends on the extent of drying; the shorter the drying time, the greater the pore size.

Preparation of Membranes

Suitable membranes should prevent the escape of colloidal material but allow rapid diffusion of solvent and small molecules. They are usually prepared by evaporation of layers of a solution of membrane material in a volatile solvent (*e.g.*, acetone, ether). The solution is cast on to either a rotating thimble-shaped mould or a flat surface. Several layers are applied and each is allowed to evaporate under controlled conditions of humidity and temperature before next one is added. The membrane is finally hardened by immersion in a liquid in which it is insoluble.

If the original solvent is non-volatile the membrane material may be deposited as a film in a support such as filter paper.

Factors Affecting Permeability

Since the structure of a membrane resembles that of a gel, the factors that effect to the permeability of membranes are similar to those that affect the rate of diffusion of substances through gel.

Solvents are used to preserve the regularity of a gel during the hardening process. These liquids cause swelling of the gel material as opposed to complete solution. They are not removed by the complete evaporation but dissolve out of the membrane into the hardening liquid.

The pore size may also be affected by various treatments after the membranes are formed. For example, stretching by means of hydrostatic pressure, partial digestion by cellulose enzymes or treatment with zinc chloride will increase the permeability of cellophane membranes, while acylation will cause a decrease in permeability.

13.7. DONNAN MEMBRANE EQUILIBRIA

The diffusion of small ions through a membrane will be affected by the presence of a charged macromolecule that is unable to penetrate the membrane because of its size. This is known as Donnan membrane effect and it may be explained by considering a system consisting of a solution of sodium chloride separated by a membrane from another solution containing a charged macromolecule (R^-) and its gegenion (Na^+). If the initial concentration of sodium chloride is c_1 and that of the macromolecule is c_2, the system may be represented diagrammatically as

$$\begin{array}{lcc:cc} \text{Initial concn.} & Na^+ + & Cl^- & Na^+ + & R^- \\ & c_1 & c_1 & c_2 & c_2 \end{array}$$

In dilute solutions, the product of the concentrations of the diffusible ions (*i.e.*, Na^+ and Cl^-) will be equal on both sides of membrane when equilibrium is established. Assuming that the condition of electroneutrality holds *i.e.* the concentrations of positively and negatively charged ions on each side of the membrane must balance. If the amount of sodium chloride that has diffused through the membrane when equilibrium has been established is x then the system may be represented as

$$\begin{array}{lcc:ccc} & Na^+ \;+ & Cl^- & Na^+ \;+ & R^- \;+ & Cl^- \\ \text{Equilibrium concn.} & (c_1-x) & (c_1-x) & (c_2+x) & c_2 & x \end{array}$$

$\therefore$ at equilibrium $(c_1-x)(c_1-x)=(c_2+x)x$

$$c_1^2-2c_1x+x^2=c_2x+x^2$$

$$c_1^2 = c_2x + 2c_1x$$

$$= x(c_2 + 2c_1)$$

$$\therefore \quad x = \frac{c_1^2}{2(c_2 + 2c_1)}$$

$$\therefore \quad \frac{x}{c_1} = \frac{c_1}{(c_2 + 2c_1)} \qquad \ldots (13.39)$$

In Equation (13.39) $\frac{x}{c_1}$ represents the fraction of sodium chloride that has diffused through the membrane when equilibrium has been established. It can be seen that this fraction is influenced by the concentration of the non-diffusible ion R^-. If the unequal distribution of diffusible electrolyte that occurs in the presence of a charged macromolecule is not taken into account then determination of osmotic pressure exerted by the macromolecule will be incorrect. However, if the concentration of diffusible electrolyte is relatively high, then the denominator on the right hand side of Equation (13.39) is approximately equal to $2C_1$. The equation then reduces to $\frac{x}{c_1} = \frac{1}{2}$ indicating that the simple electrolyte is equally distributed on both sides of the membrane and that the Donnan effect is negligible in such cases.

13.8. MEASUREMENT OF OSMOTIC PRESSURE

Frazer and Morse method. The method employs a porous vessel, *A*, in the walls of which is deposited a layer of copper ferrocyanide by some special technique which involves the passage of electricity through solutions of copper sulphate and potassium ferrocyanide separated from each other by the porous vessel. This is connected to a tube *B*. Both the vessel and the tube are filled with the solvent. The vessel is surrounded by a solution contained in the bronze cylinder *C*. Solvent will enter the solution and result in the hydrostatic pressure equal to osmotic pressure in the vessel *C*. This can be measured by a manometer attached to *C*.

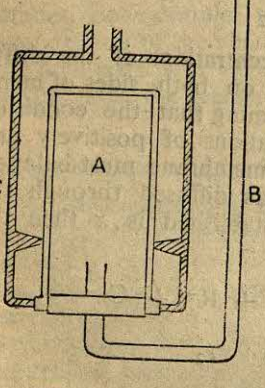


Fig. 13.11. Frazer and Morse apparatus.

Berkely and Hartley method. This is another accurate method for measuring the osmotic pressure. The solvent is placed in the horizontal tube *A*, on the sides of which a thin layer of copper ferrocyanide is deposited. This tube is placed by means of watertight joints into a metal jacket *B* which contains the solution and carries an attachment C through which pressure can be applied. A is first filled with the solvent through D up to a definite point in the capillary E. As a result of osmosis, the level of liquid in the capillary will fall but by applying pressure through C, it is restored to its initial value. This pressure is taken as the osmotic pressure of the solution.

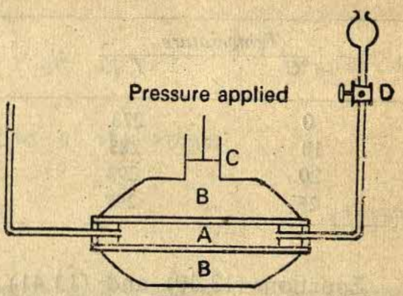


Fig. 13.12. Berkeley and Hartley apparatus.

Results of osmotic pressure measurement. The results obtained from Pfeffer's classic experiments on aqueous solutions of sucrose, presented in Table 13.1, clearly show that the ratio of the osmotic pressure (π) to the concentration *i.e.*, π/C, is approximately constant at constant temperatures. In other words, the osmotic pressure of a solution is directly proportional to its concentration at constant temperature. Further, $C \propto \frac{1}{V}$ where V is is the volume of solution containing 1 mole of the solute. Therefore, osmotic pressure of a solution is inversely proportional to volume at constant temperature. Mathematically

$$\pi \propto \frac{1}{V} \ (T=\text{Constant})$$

or

$$\pi V=\text{Constant} \quad \ldots (13.40)$$

TABLE 13.1

Osmotic pressures of sucrose solution at 0°C

Concentration gram/litre	*Osmotic Pressure* (π) (*atm*)	*Volume* (V) *containing 1 gram mole* (*litres*)	πV	π/C
10	0.70	34.20	23.94	0.70
20	1.34	17.10	22.91	0.67
40	2.74	8.55	23.42	0.685
60	4.05	5.70	23.09	0.675

Similarly it can be seen from Table 13.2, that the osmotic pressure increases with increase temperature for constant concentration of solution and the ratio, π/T is approximately constant *i.e.*,

$$\frac{\pi}{T}=\text{Constant (At constant concentration)} \quad \ldots (13.41)$$

TABLE 13.2

Effect of temperature on osmotic pressure of sucrose solutions

Temperature		*Osmotic Pressure*	π/T
$t°C$	T K	(π) (*atm*)	
0	273	7.085	0.02594
10	283	7.334	0.02591
20	293	7.605	0.02595
25	298	7.729	0.02594

Equations (13.40) and (13.41) are similar to Boyle's Law and Charle's Law respectively for gases with the only difference that the osmotic pressure, π, is taken for the gas pressure. Vant Hoff concluded from these results that there is a parallelism between the properties of solution and the properties of gases. He combined equations (13.40) and (13.41) as in the case with gases and suggested the relation,

$$\pi V = RT \qquad \ldots (13.42)$$

where R is a constant. By substituting the value of cosmotic pressure for a solution of known concentration at a definite temperature, he calculated the value of R. This came out to be almost identical with the familiar gas constant. Equation (13.42) is known as the *Van't Hoff Equation* and holds only for dilute solutions.

In equation (13.42), V is the volume of the solution containing 1 mole of the solute. If n_2 moles of the solute are dissolved in volume V of the solution, equation (13.42) becomes

$$\pi V = n_2 RT \qquad \ldots (13.43)$$

(If there are two solutions having the same osmotic pressure at the same temperature, they will have the same molar concentration. Such solutions are regarded as *Isotonic Solutions.*)

Thermodynamic derivation of Van't Hoff equation

Consider a solution in equilibrium with the solvent. If $\mu(T, P+\pi, X_1)$ is the chemical potential of the solvent in the solution under the pressure $P+\pi$ and $\mu°(T, P)$ that of the pure solvent under the pressure P, then the equilibrium condition is

$$\mu(T, P+\pi, X_1) = \mu°(T, P) \qquad \ldots (13.44)$$

or

$$\mu°(T, P+\pi) + RT\ln X_1 = \mu°(T, P) \qquad \ldots (13.45)$$

In order to express chemical potential of the solvent under a pressure $P+\pi$, in terms of chemical potential of the solvent under a pressure P, we make use of the fundamental equation according to which the increase in the chemical potential of the solvent by increasing the pressure is given by the relation

$$d\mu° = \bar{V}_0 dP \qquad \text{(Refer to Chapter 9)}$$

where $\bar{V}°$ is the molar volume of the pure solvent. On integrating, we have

$$\mu°(T, P+\pi)-\mu°(T, P)=\int_{P}^{P+\pi} \bar{V}_0 dP \qquad \ldots (13.46)$$

Substituting this result in equation (13.45); we get

$$\int_{P}^{P+\pi} \bar{V}_0 dP+RT\ln X_1=0 \qquad \ldots (13.47)$$

If it is assumed that V_0 is independent of pressure *i.e.*, the solvent is practically incompressible, we get on integration and simplification,

$$\bar{V}_0\pi+RT\ln X_1=0 \qquad \ldots (13.48)$$

This equation gives a relationship between the osmotic pressure π and the mole fraction of solvent in the solution. Another assumption involved is that the solution is ideal.

If X_2 is the mole fraction of the solute in the solution, X_1 can be replaced by $(1-X_2)$.

For dilute solution, $\ln X_1=\ln(1-X_2)\approx -X_2=\frac{-n_2}{n_1+n_2}\approx\frac{-n_2}{n_1}$

Therefore, equation (13·48) becomes

$$\bar{V}_0\pi-\frac{n_2}{n_1}RT=0$$

or

$$\pi=\frac{n_2 RT}{n_1\bar{V}_0}=CRT \qquad \ldots (13.49)$$

Again, by the addition rule, the volume of the ideal solution is

$$V=n_1\bar{V}_0+n_2\bar{V}_2\approx n_1\bar{V}_0$$

Thus, equation (13.49) becomes

$$\pi=\frac{n_2 RT}{V}=CRT \qquad \ldots (13.50)$$

where $C\left(=\frac{n_2}{V}\right)$ is the molar concentration of solute in the dilute solution.

Equation (13.50) is known as the Frazer and Morse equation for osmotic pressure.

Osmotic Pressure—A Colligative Property

From equation (13.50), we have

$$\pi=CRT$$

This equation shows that for a definite temperature, osmotic pressure depends only on the concentration of the solute and not on the nature of solute or solvent. Therefore, osmotic pressure of a solution is a colligative property.

Determination of molecular weight. Osmotic pressure measurement can be employed to obtain the molecular weight of the solute with more degree of accuracy. This can be easily done by putting $n_2=\frac{W_2}{M_2}$ in equation (13.49) where W_2 is the weight of the solute of molecular weight M_2.

Problem 13.4. A solution containing 4.0 g of a polyvinyl chloride polymer in 1 litre of dioxane was found to have an osmotic pressure of 6.4×10^{-1} atm at 27°C. Calculate the approximate molecular weight of the polymer.

Solution. The concentration of the solution is $\frac{4.0}{M}$ mole litre^{-1} where M is the required molecular weight. Since the osmotic pressure is given in atm, R is expressed in litre-atm deg^{-1} mol^{-1}, *i.e.*, 0.082, and hence by equation

$$\pi=RTC$$

we have

$$6.4\times10^{-4}=0.082\times300\times\frac{4.0}{M}$$

or

$$M=1.5\times10^{5}$$

Molecular weight of the polymer$=1.5\times10^{5}$.

13.9. RELATION BETWEEN VARIOUS COLLIGATIVE PROPERTIES

Since all colligative properties depend on the mole fraction of the solute and are independent of the individual properties of the solute, all of these must be related to each other by *a* single expression as

$$\frac{\triangle P}{P^{\circ}}=\triangle T_b\ \frac{\triangle H_v}{RT_0^2}=\triangle T_f.\ \frac{\triangle H_f}{RT_0^2}=\frac{\pi V}{RT}=X_2 \qquad \ldots (13.51)$$

This expression can be used to calculate all other colligative properties, if one colligative property is known.

Problem 13.5. The osmotic pressure of a solution containing 18.0 g. fructose per litre is 2.472 atm. at 30°C. The molar volume of water at this temperature is 18.1 cc. Calculate the boiling point of this solution.

(Heat of vaporisation of water=9720 cal/mol)

Solution. $\because \pi=\frac{\triangle H_v\,.\,T}{VT_0^2}\triangle T_b$

Here

$$\pi=2.472\times76\times13.6\times981 \text{ dynes/cm}^2$$

$$\triangle H_v=9720\times4.18\times10^7 \text{ ergs}$$

$$T_0=100+273=373 \text{ K}$$

$$V=18.1 \text{ cc.}$$

$$\triangle T_b = ? \qquad \text{and} \qquad T = 30 + 273 = 303 \text{ K.}$$

$$\therefore \quad \triangle T_b = \frac{(2.472 \times 76 \times 13.6 \times 981)(18.1)(373)^2}{(9720 \times 4{\cdot}18 \times 10^7)(303)} = 0.05126^\circ$$

$\therefore$ Boiling point of the solution $= T_0 + \triangle T_b$

$$= 100 + 0.05126^\circ = 100.05126^\circ\text{C.}$$

13.10. COLLIGATIVE PROPERTIES OF SOLUTIONS CONTAINING TWO OR MORE SOLUTES

If a solution contains two or more than two solutes, the colligative properties are given by the following equations:

(*i*) *Relative lowering of vapor pressure*

$$\frac{\triangle P}{P^0} = \left(\sum \frac{W_i}{M_i} \right) \frac{M_1}{W_1} = \frac{\Sigma m_i \times M_1}{1000} \qquad \ldots (13.52)$$

where W_i is the weight of each solute, M_i is its molecular weight and $\Sigma\, m_i$ is the total molality of the solution. M_1 and W_1, as before, are the molecular weight and the weight of the solvent.

(*ii*) *Boiling point elevation*

$$\triangle T_b = K_b \Sigma m_i \qquad \ldots (13.53)$$

where Σm_i is the total molality of the solution

(*iii*) *Freezing point depression*

$$\triangle T_f = K_f \Sigma m_i \qquad \ldots (13.54)$$

where Σm_i is again the total molality of the solution.

(*iv*) *Osmotic pressure.*

$$\pi = \Sigma\, C_i RT \qquad \ldots (13.55)$$

where ΣC_i is the total concentration of thc solution.

13.11. COLLIGATIVE PROPERTIES OF SOLUTIONS OF ELECTROLYTES

While discussing the four properties, it was assumed that solute persists in the same molecular form in the solvent. Such solutions obey the various relations deduced there. On the other hand, there are some solutes which associate or dissociate in the solvent and yield abnormal results when the various relations deduced are applied to them. Consider solutions of electrolytes such as aqueous solutions of strong acids, bases and their salts. In such solutions, the solute has a tendency to dissociate into ions, thereby, increasing the number of particles in the solutions. Consequently for such solutions, the freezing point lowering, boiling point elevation, vapor pressure lowering and osmotic pressure are higher than for non-electrolytes when solutions having the same concentrations of electrolytes and non-electrolytes are compared.

In order to account for all abnormal cases and to represent colligative properties of electrolytes by means of relations for non-electrolytes, Van't Hoff introduced the factor i, known as the *Van't Hoff factor*. This factor is defined *as the ratio of the colligative effect produced by a definite concentration of the electrolyte divided by the effect observed for the same concentration of a non-electrolyte*. Thus

$$i=\frac{\triangle T_b}{(\triangle T_b)_0}=\frac{\triangle T_f}{(\triangle T_f)_0}=\frac{\pi}{(\pi)_0}=\frac{\triangle P}{(\triangle P)_0}$$

where $(\triangle T_b)_0$, $(\triangle T_f)_0$, $(\pi)_0$ and $(\triangle P)_0$ are the boiling point elevation, freezing point depression, osmotic pressure and vapor pressure lowering respectively for solutions of non-electrolytes and similar terms used in the numerator are for solutions of electrolytes having the same concentrations.

The value of i can be calculated from experimental data for each electrolyte at various concentrations. The value, calculated for a particular concentration of an electrolyte for one of the colligative properties, is found to be same and valid for other properties at the same concentration. Thus, for solutions of electrolytes,

$$\triangle P=i\,(\triangle P)_0=iP^\circ X_B$$

$$\triangle T_f=i\,(\triangle T_f)_0=iK_f m$$

$$\triangle T_b=i\,(\triangle T_b)_b=i.K_b m$$

and $$\pi=i\,(\pi)_0=i\,\frac{nRT}{V}$$

Utilising Arrherius theory of Electrolytic dissociation, it is possible to calculate the degree of association or dissociation if the value of Van't Hoff factor is known.

Degree of association. During association, two or more molecules combine to form one molecule. The fraction of the total number of molecules which combine to form one molecule is known as the degree of association.

Consider a solute, say A, dissolved in a definite volume of solution. Let α be the degree of association and n the number of molecules which combine to form an associated molecule. If m is the original molality of the solution, equilibrium is represented by:

$$\begin{array}{cc} m & 0 \\ nA \rightleftharpoons & (A)_n \\ m(1-\alpha) & m\alpha/n \end{array}$$

The number of simple (unassociated) molecules left

$$=m(1-\alpha)$$

The number of associated molecules formed

$$=\frac{m\alpha}{n}$$

Therefore, the total number of particles, m_t in solution is given by

$$m_t=m\left(1-\alpha+\frac{\alpha}{n}\right) \qquad \dots (13.56)$$

For a total molality m_t, the freezing point depression is given by

$$\triangle T_f=K_f.m_t$$

Hence, equation (13.56) becomes

$$\triangle T_f=K_f m\left(1-\alpha+\frac{\alpha}{n}\right) \qquad \dots (13.57)$$

Further, Van't Hoff factor, i is given by

$$i=\frac{\triangle T_f}{(\triangle T_f)_0} \text{ or } \triangle T_f=i(\triangle T_f)_0$$
$$=iK_f m \qquad \dots (13.58)$$

Substituting this value in equation (13.57), we get

$$iK_f m=K_f m\left(1-\alpha+\frac{\alpha}{n}\right)$$

or

$$i=1-\alpha+\frac{\alpha}{n}$$

Simplifying for α,

$$\alpha=\frac{i-1}{\frac{1}{n}-1} \qquad \dots (13.59)$$

Knowing i and n, α can be easily calculated from equation (13.59).

Degree of dissociation. It is defined as the fraction of the total number of molecules which dissociate into electrically charged particles called *ions*.

Consider an electrolyte, A_xB_y, dissolved in some solvent. Let m is the molality of the solution and α is the degree of dissociation. The dissociation of the electrolyte is represented by the equilibrium

$$\begin{array}{ccc} m & o & o \\ A_xB_y \rightleftharpoons & xA^+ & +\ yB^- \\ m(1-\alpha) & mx\alpha & my\alpha \end{array}$$

The total number of moles, m_t, of all types in the solution

$$m_t=m(1-\alpha)+mx\alpha+my\alpha$$
$$=m[1+\alpha(x+y-1)] \qquad \dots (13.60)$$

Let n is the total number of ions yielded by a molecule of the electrolyte *i.e.*, $n=x+y$

Equation (13.60) becomes

$$m_t=m[1+\alpha(n-1)] \qquad \dots (13.61)$$

Again, freezing point depression for a total molality M_t, is given by

$$\triangle T_f = K_f m_t$$

Therefore, $\triangle T_f = K_f m[1+\alpha(n-1)]$ . . . (13.62)

Further, $\triangle T_f = i(\triangle T_f)_0 = iK_f m$

Hence, equation (13.62) becomes

$$iK_f m = K_f m[1+\alpha(n-1)]$$

or $\alpha = \dfrac{i-1}{n-1}$ . . . . (13.63)

Equations (13.59) and (13.60) for degree of association and degree of dissociation, respectively, can also be derived from boiling point elevation, vapor pressure lowering or osmotic pressure. In every case, the value of i comes out to be the same.

Problem 13.6. A molecule of a substance XY (Mol. Wt. 180) undergoes second order association in water. If the Van't Hoff factor, i, of the substance is 0.88, what is the degree of association of the substance?

Solution. We get association of XY as

$$2XY \rightleftharpoons (XY)_2$$

If α be the degree of dissociation, then we have at equilibrium,
moles of XY unassociated $=2-2\alpha$ and moles of $(XY)_2=\alpha$

$\therefore$ Total number of moles at equilibrium $=2-2\alpha+\alpha=2-\alpha$.

Since $\alpha = \dfrac{i-1}{\dfrac{1}{n}-1}$

Substituting the various values, we have

$$\alpha = \frac{0.88-1}{\dfrac{1}{2}-1} = \frac{0.12}{-0.5} = 0.24$$

$\therefore$ Degree of association $\alpha = 24\%$.

Problem 13.7. A 0.9% salt solution is isotomic with blood cells. What is the osmotic pressure of this solution at 37°C? Assume that the salt is fully dissociated.

Solution.

$$\pi V = nRT$$

$$\pi = ?$$

$$V = 0.1 \text{ litre}$$

$$n = \frac{0.9}{58.5} \times 2$$

$$R = 0.082 \text{ litre-atm deg}^{-1} \text{ mole}^{-1}$$

$$T = 300\text{K}$$

$$\pi \times 0.1 = \frac{2 \times 0.9}{58.5} \times 0.082 \times 310$$

$$\pi = 7.81 \text{ atm.}$$

Problem 13.8. A 0.1 formal solution of sodium chloride is found to be isotonic with a 1.10% solution of urea. Calculate the apparent degree of dissociation of sodium chloride.

Solution. Since the observed osmotic pressure of 0.1 F NaCl is that of 1.1% urea solution.

Conc. of urea,

$$C=\frac{1,1}{60}\times\frac{1}{0.1}=0.183 \text{ mole/litre}$$

Osmotic pressure of urea solution, $\pi=0.183\ RT$

$$i=\frac{0.183}{0.1}=1.83$$

For dissociation of NaCl $n=2$

Apparent degree of dissociation 0.1° F NaCl solution

$$\alpha=\frac{(i-1)}{x-1}=\frac{0.83}{1}$$

or $$83\%.$$

PROBLEMS

1. (*a*) State Raoult's law for relative lowering of vapor pressure. Explain how it can be used for determining the molecular weight of a dissolved non-volatile substance.

(*b*) The vapor pressure of a solution containing 13 g of solute in 100 gm of water at 28°C is 27.371 mm. Calculate the molecular weight of the solute. The vapor pressure of water at the temperature is 28.065 mm.

(Ans. 94.6)

2. Vapor pressure lowering is a colligative property, *i e.*, it is a property which depends only on the number of solute particles in solutions and not on the nature of these particles. Explain.

3. The vapor pressure of water at 20°C is 17.0 mm. Calculate the vapor pressure of a solution of 3 g of urea in 50 g of water. Molecular weight of water is 18 and that of urea is 60.

(Ans. 16.69 mm)

4. (*a*) Will the normal boiling point of an aqueous solution and pure water be the same? Why?

(*b*) 'Boiling point elevation' is a colligative property. Explain.

5. What is ment by elevation of boiling point? How is it related to the degree of dissociation and molecular weight of a solute?

6. (*a*) Describe Landsberger's method for finding the elevation in the boiling point of a solvent on dissolving a non-volatile solute in it.

(*b*) The molal boiling point elevation constant K_b for CCl_4 is 5·02 deg/mol. The boiling point of pure CCl_4 is 76.8°C. Calculale the boiling point of a 1.0 molal solution of naphthalene, $C_{10}H_8$ in CCl_4

(Ans. 81.8°C)

7. Calculate the value of K_b for chloroform, $CHCl_3$, from the following data:

Boiling point of pure $CHCl_3=61.3°C$.

(*a*) A solution containing 5.02 g of naphthalene, $C_{10}H_8$ in 18.0 g of $CHCl_3$ boils at 69.5°C.

(Ans. 3.8 deg/molal)

(*b*) The boiling point of chloroform was raised by 9.325°C when 0.5141 g of anthracene was dissolved in 35 g of chloroform. Calculate the molecular weight of anthracene (K = 39.0° per 100 g of $CHCl_3$.

(**Ans.** 176.2 a.w.u.)

8. What point corresponds to the freezing point of pure water at 1 atm pressure? How does the vapor pressure lowering affect the freezing point of the solution?

9. (*a*) What is meant by Cryoscopic-Constant? Explain how the depression of freezing point of a solvent may be used to determine the molecular weight of the dissolved substance.

(*b*) The freezing point of pure camphor is 178.4°C and its molal freezing point constant is 40.0 m^{-1}. Find the freezing point of a solution containing 1.50 gram of a compound of molecular weight 125 in 25.0 gram of camphor.

(**Ans.** 13.7°C)

10. (*a*) What is meant by molecular depression of freezing point of a solvent? Give an experimental method for its determination.

(*b*) A solution made by dissolving 4.0 g of an organic solute *A* in 50.0 g of benzene freezes at 3.74°C. K_f for benzene = 5.12° C/molal, freezing point of pure benzene = 5.48°C. Calculate the molecular weight and molecular formula of *A*. The empirical formula of *A* is C_3H_2Br.

(**Ans.** $C_6H_4Br_2$)

11. 6.0 g of anydrous magnesium sulphate are dissolved in 100 g of water. The depression of the freezing point is 0.910°C. If the constant for water in the case of electrolyte is 37, what formula represents the state of hydration of the dissolved salt?

(**Ans.** $MgSO_4.7H_2O$)

12. State the laws of osmotic pressure. Explain how the osmotic pressure is analogous to gas pressure. How can the molecular weight of a substance in solution be determined from its osmotic pressure?

13. (*a*) An aqueous solution of glucose, $C_6H_{12}O_6$, has an osmotic pressure of 2.72 atm at 298K. How many moles of glucose were dissolved per litre of solution?

(**Ans.** 0.11 mol/litre)

(*b*) The osmotic pressure of a solution of a synthetic polyisobutylene in benzene was determined at 25°C. A sample containing 0.20 g of solute per 100 ml of solution, developed a rise of 2.4 mm at osmotic equilibrium. The density of the solution was 0.88 g/cc. What is the molecular weight of the polyisobutylene?

(**Ans.** 2.4×10^5g/mole)

14. (*a*) Describe a method for the determination of osmotic pressure of dilute solutions. Explain the term 'isotonic' solution.

(*b*) A solution of non-electrolyte having molecular weight of 60 and containing 11 gm of the compound per litre was found to be isotonic with a decinormal solution of sodium chloride. What is the apparent degree of ionization of the electrolyte?

(**Ans.** 83.33 per cent)

15. (*a*) KBr is 79.0 per cent dissociated in solution. What is the freezing point of a 0.500 molal aqueous solution? (**Ans.** $T_f = -1.66$°C)

(*b*) A 0.100 molal solution of acetic acid in water freezes at 0.190°C. Calculate the per cent dissociation of acetic acid at this temperature.

(**Ans.** 2 per cent)

16. If a solution of mercuric cyanide containing 3 g per litre has an osmotic pressure of 232 mm Hg at 25°C, what is the apparent molecular weight and the degree of dissociation of mercuric cyanide?

(Ans. 252.6 a.w.u.; 2.6%)

17. Write notes on the following:

(*a*) Vant't Hoff Theory of dilute solutions.

(*b*) Theory of Osmosis.

(*c*) Abnormal Colligative properties.

Chapter 14

ELECTROCHEMISTRY

14.1. INTRODUCTION

Electrochemistry is concerned with the chemical transformations produced by the passage of electricity and with the production of electricity by means of chemical transformations. The fact that electricity can be produced by means of chemical reactions allows the storage of electrical energy in the form of chemical reagents which may be used to produce electrical energy at a more convenient time or place. The phenomena encountered in electrochemistry are of great theoretical and practical importance.

14.2. OHM'S LAW AND ELECTRICAL UNITS

According to Ohm's Law, the strength of an electric current flowing through a conductor, *i.e.*, the quantity of electricity flowing per second (I) is directly proportional to potential difference (E) applied across the conductor and is inversely proportional to the resistance (R) offered by the conductor to the current *i.e.*,

$$I=\frac{E}{R} \qquad \ldots (14.1)$$

By making appropriate choice of units, the constant of proportionality is made unity.

According to the international system, the units of current, resistance, and potential are *ampere*, *ohm*, and *volt* respectively.

The international ampere is defined as the invariable current of such strength which on passage through a water solution of silver salt will deposit 1.11800 milligrams of silver in 1 second.

The international ohm is defined as the resistence at 0°C of a column of mercury of uniform cross-section, 106.300 cm long, and containining 14.4521 g of mercury.

The international volt is defined as the potential difference required to send a current of one ampere through a resistance of 1 ohm.

The quantity of electricity is measured in international *coulomb*. It is the quantity of electricity passing through a conductor when a current of 1 ampere flows in 1 second. Since the quantity of electricity carried by a current must equal rate of transport times the time, the charge Q carried by a current I in t seconds, is given by

$$Q=I.\,t \qquad \ldots (14.2)$$

Another unit of quantity of electricity is the *Faraday*. A Faraday is equal to 96,500 coulombs. The main significane of Faraday is that it is the amount of charge that produces one equivalent of chemical change.

The electrical work W performed when a current of strength I passes for t sec through a resistance across which the potential difference is E is given by Joule's law, namely,

$$W=EIt=EQ \qquad \ldots (14.3)$$

where W is expressed in *Joules*. The *Joule* is the electrical unit of energy. It is defined as the amount of work performed by a current of 1 ampere flowing for 1 sec under a potential drop of 1 volt. The conversion of work in joules to other energy units can be readily carried out through the relations

$$1 \text{ Joule}=1\times10^7 \text{ ergs}=0.2390 \text{ cal.} \qquad \ldots (14.4)$$

The rate at which work is being done by an electric current is expressed in *watts*. A *watt* is work performed at the rate of 1 Joule per second and is a unit of electrical power. It follows from equation (14.3) that the power in watts p delivered by a current is

$$p=EI=\frac{EQ}{t} \qquad \ldots (14.5)$$

A kilowatt, which is a larger unit of power, is equal to 1000 watts.

14.3. ELECTROLYTIC CONDUCTION

Electricity flows through a conductor due to transfer of electrons from a point of higher negative potential to one of lower. However, the mechanism by which this transfer takes place is different for all conductors. There are, first, the *metallic conductors* or *electronic conductors* in which the conduction takes place by direct migration of electrons through the conductor under the influence of an applied potential. Metals are typical examples of such conductors. Certain solid salts *e.g.*, lead sulphide, cadmium sulphide, copper sulphide also belong to this category.

Conducting materials of the second type are known as *electrolytic conductors* or *electrolytes*. In this type, electron transfer takes place by a migration of ions, both positive and negative, towards the electrodes on applying an electrical potential. Solutions of strong and weak electrolytes, fused salts and also some solid salts like AgI, LiH, NaCl are some examples of electrolytes. Passage of an electric current through an electrolyte is always accompanied by a transport of matter from one part of the conductor to another. Further, this transport is always manifested by chemical changes at the electrodes which are quite characteristic and specific for the substances composing the conductor and the electrode. In certain conductors known as *mixed conductors*, both electronic and ionic conduction take place. β-Ag$_2$S, CuCl, γ-Cu Br, solution of sodium in liquid ammonia are examples of mixed conductors. In such cases, the ratio of electronic to ionic conductors varies with the concentration. The main distinction between the two lies in their behaviour with respect to temperature. The resistance of electronic conductors increases while that of electrolytic conductors always decreases when the temperature is increased.

In order to understand the mechanism by which an electric current passes through a solution, consider a cell, composed of two thert metallic rods (or carbon), called *electrodes*, connected to the two terminals (*i.e.*, +and−) of the battery and immersed into an aqueous solution of sodium chloride (electrolyte). The electrode connected to the positive side of the battery is called the positive electrode or *anode* and the electrode, connected to the negative side of the battery is known as negative electrode or *cathode*. The electrons from the battery enter the solution through the cathode and leave the solution to return to battery at the anode. The electrically charged atoms or radicals that move to the electrodes are called ions. The ions which move to the cathode are known as *cations* and the ions travelling towards the anode are known as *anions*. A labelled diagram of a typical electrolytic cell is given in Fig. 14.1.

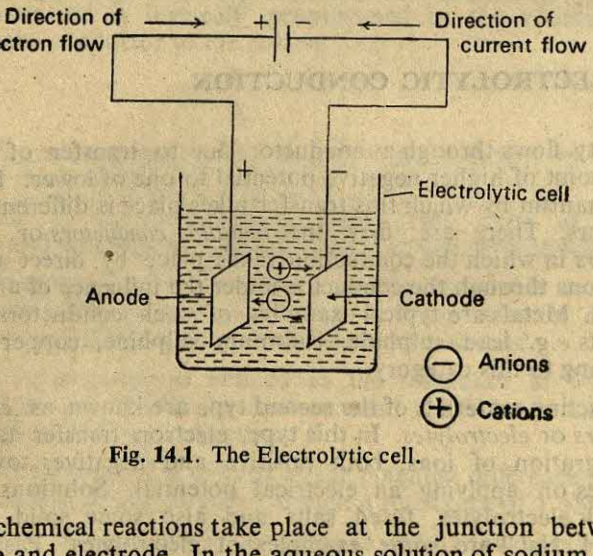


Fig. 14.1. The Electrolytic cell.

Electrochemical reactions take place at the junction between the electrolyte and electrode. In the aqueous solution of sodium chloride under consideration, we have sodium and chloride ions, and also some hydrogen and hydroxyl ions due to feeble dissociation of water. When the circuit is closed and a current passes through the solution, it is observed that chlorine is evolved at the anode while hydrogen is evolved at the cathode. Sodium ions remain as such in solution and combine with hydroxyl ions to form sodium hydroxide in the solution immediately adjacent to the cathode. Following reactions take place at the electrodes: Hydrogen ions, carrying a positive charge, reach the cathode and combine with electrons entering the solution from the cathode, thus having the charge neutralised. This results in the formation of monoatomic hydrogen. Two atoms of hydrogen thus deposited on the electrode combine then to form a molecule of hydrogen which escapes from the electrode as a gas. The reactions taking place at the cathode can be represented by

$$2H^+ + 2e^- = 2H$$

$$2H = H_{2(g)}$$

Similarly, chloride ions, which are negatively charged, reach the anode, give up the electrons to the anode, become neutral chlorine atoms and escape as a gas. The electrons thus liberated at the anode flow through the external circuit to the source of potential. The reactions here are

$$2Cl^- = 2Cl + 2e^-$$

$$2Cl = Cl_{2(g)}$$

It should be noted that two electrons are removed from the cathode to form a molecule of hydrogen, and at the same time two electrons are given up to the anode by chloride ions to form a molecule of chlorine. The net result is a transfer of two electrons from the cathode side of the circuit to the anode side.

14.4. FARADAY'S LAWS AND ELECTROCHEMICAL EQUIVALENTS

Michael Faraday (1832) made a quantitative study of the relation between the amount of electrolysis produced by the current and the quantity of electricity. His conclusions may be expressed in the form of two Laws of electrolysis:

Faraday's first law. According to this law, the mass of a substance involved in any reaction at the electrodes is directly proportional to the quantity of Electricity passed through the electrolytic solution.

Or mathematically:

$$m \propto Q$$

$$\propto ct \qquad (Q = ct)$$

or $$m = Zct. \qquad \ldots (14.6)$$

where m is the mass of the ion liberated, when a current of strength

c amperes passes for t seconds. Z is a proportionality constant and is called the *electro-chemical equivalent*.

From equation (14.6), if $c=1$ ampere and $t=1$ second, then

$$m=Z$$

Hence, the electro-chemical equivalent of an ion may be defined as the mass of the ion deposited by the passage of one ampere current for one second.

Electrochemical equivalents of some substances like copper, silver and hydrogen are 0.0003292, 0.001118 and 0.00001036 respectively.

This law is rigidly valid when the passage of electricity takes place mainly by electrolytic conductance and is independent of temperature, pressure and the nature of the solvent.

Faraday's second law. According to it, "The weights of different substances produced by the same quantity of electricity are proportional to the equivalent weights of the substances." The law can also be stated as:

"The same quantity of electricity will produce chemically equivalent quantities."

The equivalent-weights mentioned in the Faraday's law is the formula weight or atomic weight of the substance divided by the number of electrons occurring with one formula of the substance in an electrode reaction.

If the same current is passed for the same time through solutions of copper sulphate and silver nitrate (Fig. 14.2), the amounts of copper and silver deposited at the cathode are proportional to their chemical equivalents *i.e.*, 31.78 and 107.8 respectively.

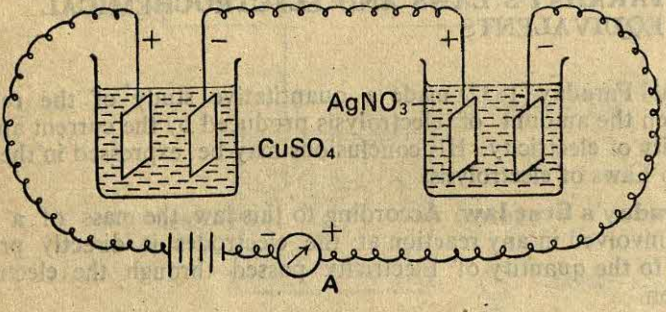


Fig. 14.2.

For example, in a solution containing cuperic ion, the electrode reaction is:

$$Cu^{2+}+2e^{-}\rightarrow Cu$$

Since two electrons change occurs in this reaction and also copper is bivalent, the equivalent weight of copper for this reaction will be atomic weight divided by two *i.e.*,

$$\frac{63.56}{2} \text{ g or } 31.78 \text{ g}$$

For a solution of silver ion, the reaction is:

$$Ag^{+} + e^{-} \rightarrow Ag$$

In this reaction, one electron change occurs and since silver is univalent, the equivalent weight of silver will be its atomic weight *i.e.*, 107.89. Since the quantity of electricity on an electron is 1.602×10^{-19} coulombs; Faraday's laws enable us to calculate the number of electrons conveying one Faraday of electricity. This is given by:

$$\frac{96{,}500}{1.602 \times 10^{-19}} = 6.023 \times 10^{23}$$

This quantity, 6.023×10^{23} is known as Avogadro's number. This means that when one Faraday of electricity is passed through the solution, Avogadro's number of electrons is supplied to the anode by oxidation of one equivalent of substance and these electrons in turn bring about the reduction at the cathode. These two processes together transfer Avogadro's number of electrons from cathode to the anode. Faraday's laws thus establish a relation between an electric current and chemical changes in the electrolytes.

Problem 14.1. A constant current was passed through a solution of $AuCl_4^-$ ions between gold electrodes. After a period of 10.00 min, the cathode increased in weight by 1.314 gram. How much charge was passed and what was the current I?

Solution. At the cathode the reduction of gold III to gold metal proceeds as follows:

$$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$$

$$\text{Moles of Au} = \frac{1.314\text{g Au}}{197\text{g/mole Au}} = 6.67 \times 10^{-3} \text{ mole Au}$$

$$q = (6.67 \times 10^{-0} \text{ mole Au}) \left(\frac{3 \text{ mole electron}}{\text{mol Au}} \right)$$

$$= 2.00 \times 10^{-2} \text{ Faraday}$$

$$\therefore \quad 1 = q/t (200 \times 10^{-2}\ F)\ (96{,}500\ C/F)/600 \text{ s.}$$

$$= 3.22 \text{ Ampere.}$$

14.5. ELECTROLYTIC CONDUCTANCE

Electrolytes are also conductors of electricity. The electrical conductance of an electrolyte is due to the ions it contains. The greater the concentration of ions, the higher will be the conductance. To compare the conductivity of different solutions, the size of the electrodes and the distance between the electrodes must be standardised. It has been found that the resistance offered by a solution is directly proportional to the distance between the electrodes and inversely proportional to the cross-sectional area of the solution between the electrodes. The resistance R is thus given by:

$$R=\rho\left(\frac{l}{a}\right) \qquad \ldots (14.7)$$

where, l is the distance between the electrodes, a is the area of cross-section and ρ is the constant of proportionality known as the specific resistance.

In equation (14.7) if $l=1$ cm

and $a=1$ sq cm, then

$\rho=R$

Hence the specific resistance is the resistance in ohms of a solution kept between electrodes 1 cm apart and area between electrodes being one square centimetre.

The reciprocal of resistance is defined as conductance, if we denote this by L, then

$$L=\frac{1}{R} \qquad \ldots (14.8)$$

It is measured in ohm^{-1} or mho. The reciprocal of specific resistance is defined as specific conductance. It is given by κ (Kappa) *i.e.*,

$$\kappa=\frac{1}{\rho}=\left(\frac{l}{a}\right)\times\frac{1}{R} \qquad \ldots (14.9)$$

It is the conductance of a solution between electrodes, 1 cm^2 in area and 1 cm apart. Specific conductance is measured in units of $\text{ohm}^{-1}\ \text{cm}^{-1}$ and is a property of conducting medium.

14.6. EQUIVALENT AND MOLAR CONDUCTANCE

In dealing with solutions of electrolytes we define a quantity known as equivalent conductance (Λ). It represents the conducting power of all ions produced by one gram equivalent of electrolyte in solution. The equivalent conductance of an electrolyte may be defined as the conductance of a volume of solution containing one gram equivalent of dissolved substance, the solution being placed between two parallel electrodes, 1 cm apart, and large enough to contain in between them all of the solution. Let v c.c. is the volume of solution containing 1 g equivalent of an electrolyte and let κ be the specific conductance of the solution. The equivalence conductance λ (lambda) will then be:

$$\lambda=\kappa v \qquad \ldots (14.10)$$

If C is the concentration of a solution in gram equivalent per litre, the volume v of the solution containing one gram equivalent will be $\frac{1000}{C}$. The equation (14.10) then becomes:

Equivalent conductivity,

$$\Lambda=\frac{1000\ \kappa}{C} \qquad \ldots (14.11)$$

Units of equivalent conductance:

Since Λ is given by

$$\Lambda=\kappa v$$

and
$$\kappa=\left(\frac{1}{a}\right)\cdot\frac{1}{R}$$

$\therefore$
$$\Lambda=\left(\frac{l}{a}\right)\frac{1}{R}\cdot v$$

$$\Lambda=\frac{(\text{cm})\times 1\times(\text{cm})^3}{(\text{cm})^2\times\text{ohm}\times\text{equiv}}$$

$$\Lambda=\text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}.$$

Therefore, units of equivalent conductance are $\text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$.

Molecular conductance (μ) is defined as the conductance of a volume of solution containing one mole of solute, the solution being placed between the two electrodes 1 cm apart and large enough to contain in between them all the solution. It is equal to the specific conductance multiplied by that volume of solution in c.c. which contains one gram molecule of the electrolyte.

If C is the concentration in moles per litre then

$$\mu=\kappa v \qquad \ldots (14.12)$$

or
$$\mu=\frac{1000}{C}\times\kappa$$

The units of molar conductance are $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$.

For an electrolyte containing two univalent ions, Λ and μ are identical.

14.7. EXPERIMENTAL DETERMINATION OF EQUIVALENT CONDUCTANCE

The method for the experimental determination of equivalent conductance lies in the determination of specific conductance of the solution. This can be done by measuring the resistance of the solution and using equation (14.9). The following steps are involved.

(1) The determination of (l/a) for the given cell. This quantity is known as the cell constant, k. An indirect method is employed for

the determination of cell constant. Solutions of potassium chloride of concentration 1.0 D, 0.1 D or 0.01 D are employed for this purpose as the specific conductance of KCl solutions at these concentrations have been very accurately determined. Here D stands for demal and 1 demal solution implies that 1.0 mole of KCl is contained in a cubic decimeter of solution at 0°C.

(2) The determination of the resistance R: The resistance of the given solution of electrolyte is determined with the help of a wheat stone bridge. A general arrangement of the apparatus is shown in Fig. 14.3. R_x is the resistance box. D is the device used for detecting the balance point. Earphones which were used earlier have now been replaced by cathode-ray oscilloscope.

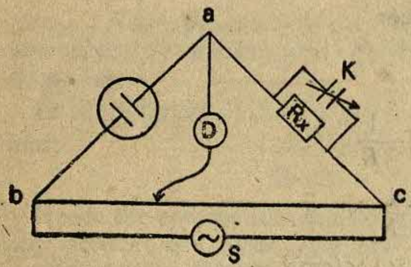


Fig. 14.3. Measurement of resistance of electrolyte.

The solution of the substance is prepared in conductance water, obtained by distilling water under reduced pressure. Kohlrausch used the water that was obtained by distilling the ordinary water forty-two times under reduced pressure. It had a specific conductance of 0.043×10^{-6} ohm^{-1} cm^{-1}.

Alternating current of low intensity is used in all conductance measurements usually of 1000-2000 cps. A direct source of current cannot be used as it sets up an E.M.F. of polarisation which tends to oppose the flow of current. The conductivity cells of various shapes have been used from time-to-time. The one used quite often is shown in Fig. 14.4.

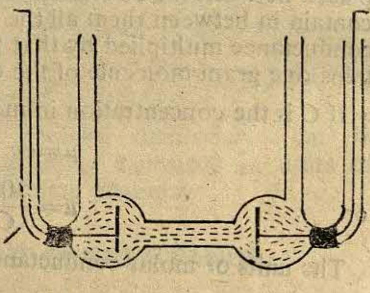


Fig. 14. 4. Cell for the measurement of conductance.

It is made of pyrex glass having the platinised platinum electrodes. Let R be the resistance of the solution. From the wheat-stone bridge equation at the balance point, we can write:

$$\frac{R}{bd}=\frac{R_x}{cd} \qquad \ldots (14.13)$$

The volume v of the solution containing 1 gm equivalent of electrolyte can be found out by analysing the given volume of the electrolyre.

Problem 14.2. The measured resistance of a cell containing exactly 0.1 g equivalent of KCl in 1000 ml at 25°C was found to be 3468.9 ohms; the specific conductance of this solution is known to be 0.012856 ohm^{-1} cm^{-1} at 25°C.

An exactly 0.1 N solution of another substance in the same cell had a resistance of 4573.5 ohms. Calculate the equivalent conductance of this electrolyte at the given concentration. (The conductance of the water is so small that it may be neglected.)

Solution. For the KCl solution, resistance (R) is $=3468.9$ ohms.

The specific conductance $(k)=0.012856$ and hence the cell constant, K is given by

$$K=k.R.=0.012856\times 3468.9=44.597 \text{ cm}^{-1}$$

Hence for the other electrolyte, the specific conductance k is given by

$$\kappa=\frac{K}{R}=\frac{44.597}{4573.4}=0.009751 \text{ ohm}^{-1} \text{ cm}^{-1}.$$

The equivalent conductance is given by equation

$$\Lambda=1000k/C$$

since the solution is exactly 0.1 N, it follows that C is 0.1000 equiv./litre and hence

$$\Lambda=\frac{1000\times 0.009751}{0.1000}=97.51 \text{ ohm}^{-1} \text{ cm}^{-2}.$$

14.8. APPLICATION OF CONDUCTANCE MEASUREMENTS

The conductance of an electrolyte becomes smaller as the solution is progressively diluted. On the other hand, the molecular and equivalent conductivities increase with dilution until a limiting value is reached. Strong electrolytes, the salt of the acids like hydrochloric, nitric and sulphuric, have high values of equivalent conductivities which increase only moderately with increasing dilution. The weak electrolytes like acetic acid and other organic acids have much lower equivalent conductivities at high concentrations, but the values greatly increase with increasing dilution. This is shown in Fig. 14.5.

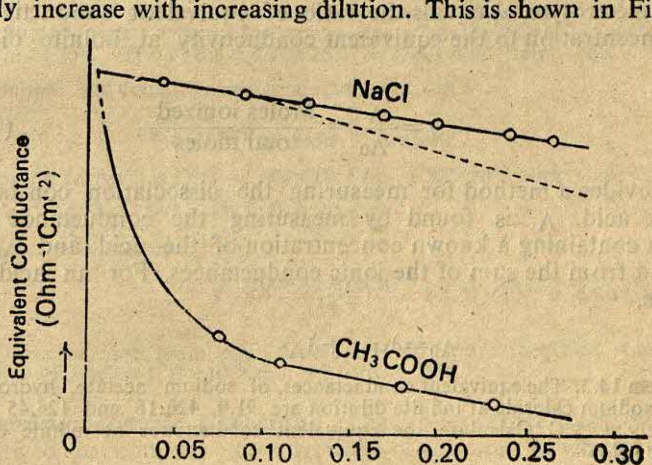


Fig. 14.5. Equivalent conductances of strong and weak electrolytes.

Kohlrausch gave an empirical relationship between the equivalent conductance Λ_0 of an electrolyte and equivalent ionic conductivities of the anions and of the cations.

$$\Lambda_0=\lambda^{+}_{0}+\lambda^{-}_{0} \qquad \ldots (14.14)$$

where λ^{+}_{0} and λ^{-}_{0} are the ionic conductivities at infinite dilution. This is known as the Kohlrausch's law of independent migration of ions.

Table 14.1 lists the values of ionic conductances of the anions and the cations.

TABLE 14.1.

Equivalent ionic conductances at infinite dilution at 25°C.

	Ions	
Cations	K^+	73.52
	Na^+	50.11
	Li^+	38.69
	H^+	349.82
Anions	Cl^-	76.34
	Br^-	78.40
	NO_3^-	71.44
	$\frac{1}{2}SO_4^-$	79.80

The conductance ratio. At any concentration, the fraction of ionised electrolyte, α, equals the ratio of equivalent conductivity at that concentration to the equivalent conductivity at infinite dilution *i.e.*,

$$\alpha=\frac{\Lambda}{\Lambda_0}=\frac{\text{Moles ionized}}{\text{total moles}} \qquad \ldots (14.15)$$

This provides a method for measuring the dissociation constant of a weak acid. Λ is found by measuring the conductance of a solution containing a known concentration of the acid and Λ_0 can be found from the sum of the ionic conductances. For an acid HA, we have.

$$\Lambda_0=\lambda_{H^+}+\lambda_{A^-}$$

Problem 14.3. The equivalent conductances, of sodium acetate, hydrochloric acid and sodium chloride at infinite dilution are 91.0, 426.16 and 126.45 ohm^{-1} respectively at 25°C. Calculate the equivalent conductance at infinite dilution for acetic acid:

Solution.

$$\lambda^{\circ}{}_{CH_3COONa}=\lambda^{\circ}{}_{CH_3COO^-}+\lambda^{\circ}{}_{Na^+}=91.0\ ohm^{-1}$$

$$\lambda^\circ_{HCl}=\lambda^\circ_{H^+}+\lambda^\circ_{Cl^-}=426.16\ \text{ohm}^{-1}$$

$$\lambda^\circ_{NaCl}=\lambda^\circ_{Na^+}+\lambda^\circ_{Cl^-}=126.45\ \text{ohm}^{-1}$$

$$\lambda^\circ_{CH_3COO^-}+\lambda^\circ_{H^+}=\lambda^\circ_{CH_3COO^-}+\lambda^\circ_{Na^+}+\lambda^\circ_{H^+}+\lambda^\circ_{Cl^-}-\lambda^\circ_{Na^+}-\lambda^\circ_{Cl^-}$$

or

$$\lambda^\circ_{CH_3COOH}=\lambda^\circ_{CH_3COONa}+\lambda^\circ_{HCl}-\lambda^\circ_{NaCl}$$
$$=91.0+426.16-126.45=390.71$$

Equivalent conductance of acetic acid at infinite dilution is 390.71 ohm^{-1} at 25°C.

Determination of solubilities of sparingly soluble salts. Several sparingly soluble salts in water, *e.g.*, $BaSO_4$, AgCl, PbS etc., ionise in a simple manner and for many purposes these may be regarded as insoluble. If S is the solubility of a given salt in gram equivalent per litre and κ is the specific conductance of the saturated solution, the solution being very dilute, the equivalent conductance will be

$$\Lambda_0=\frac{1000\ \kappa}{S} \qquad \ldots (14.16)$$

Hence the solubility,

$$S=\frac{1000\kappa}{\Lambda_0} \qquad \ldots (14.17)$$

Thus taking the value of Λ_0 from the table of limiting equivalent conductances , the solubility S can be calculated.

Problem 14.4. For a saturated solution of AgCl at 25°C, κ was fouud to be $3.41\times10^{-6}\ \text{ohm}^{-1}\ \text{cm}^{-1}$. The value of K for water used to make up the solution was $1.60\times10^{-6}\ \text{ohm}^{-1}\ \text{cm}^{-1}$. Determine the solubility of AgCl in water in moles per litre at 25°C. The λ° for AgCl at 25°C is 138.3 $\text{ohm}^{-1}\ \text{cm}^{-1}\ \text{equiv.}^{-1}$

Solution. The actual specific conductance of AgCl

$$\kappa_{AgCl}=\kappa_{solution}-\kappa_{water}$$

Hence κ forAgCl is $(3.41-1.60)\times10^{-6}$ *i.e.*, $1.81\times10^{-6}\ \text{ohm}^{-1}\ \text{cm}^{-1}$

The λ° AgCl at 25°C is 138.3 $\text{ohm}^{-1}\ \text{cm}^{-1}$.

Hence, by equation (14.15).

$$S=\frac{1000\times1.81\times10^{-6}}{138.3}=1.31\times10^{-5}\ \text{g. equiv. per litre},$$

In this case, since gram equivalents and moles are identified, therefore the solubility of AgCl is 1.31×10^{-5} mol per litre at 25°C.

Conductometric titrations. The conductance method can be employed to conduct the titrations of solutions in which there is a significant difference in specific conductance between the original solution and the reaction mixture after adding the titrant. The method involves the study of the variation of electrical conductivity of the solution during the course of titration. The conductance produced by any ion is proportional to its concentration (keeping the temperature constant). In some cases, the conductance does not show a linear relationship with the concentration due to hydrolysis of reactants or products or partial solubility of a precipitated product.

The relationship between the chemical reaction occuring during titration and the shape of the resulting curves have been discussed below in details:

Acid-base Titrations

(*a*) **Strong acid** vs **strong base**. Consider the reaction in which a strong alkali, *e.g*,, 0 1 N NaOH is added to a solution of strong acid *e.g* , 0.01 N HCl.

The reaction can be symbolised as follows:

$$(H^+ + Cl^-) + (Na^+ + OH^-) \longrightarrow Na^+ + Cl^- + H_2O$$

The highly conducting hydrogen ions present initially in the solution are replaced by sodium ions having a much smaller conductance whereas the concentration of chloride ions remains constant. Consequently, the conductivity of the solution diminishes. After the equivalence point, the further addition of sodium hydroxide results in an increase of conductance since the hydroxyl ions are no longer consumed in the chemical reaction.

Figure 14.6 (*a*) shows the graph produced in the above case. It consists of two straight lines intersecting at the equivalence point. If there is little volume change during the titration, the lines are practically straight lines. It is for this reason that alkali should be about 10 times as strong as the acid in order to keep the volume change small.

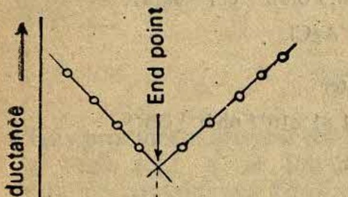


Fig. 14.6. (*a*) Conductance titration of strong acid and strong alkali (say 0.1 N-NaOH vs 0.01 N-HCl).

(*b*) **Strong acid** vs **weak base**. When a strong acid is titrated against a weak base *e.g*., NH_4OH, the first part of the curve is similar to strong acid vs strong base titration, as both are strong electrolytes. But after the equivalence point, the conductance does not vary so much, as the free base behaves like weak electroyte and its conductance is very small as compared with that of the acid or its salt. The shape of curve is as shown in Fig. 14.6 (*b*).

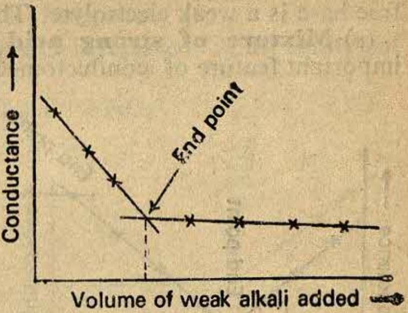


Fig. 14.6. (*b*) Conductance titration of strong acid and weak alkali (*e.g.* 0.1 N NH_4OH vs. 0.01 N HCl).

(*c*) **Weak acid** vs **strong base**. When a weak acid *e.g.*, acetic acid is titrated with a solution of strong alkali *e.g.*, NaOH, the reaction proceeds as:

$$(CH_3COO^- + H^+) + (Na^+ + OH^-) \longrightarrow CH_3COONa + H_2O$$

The curve obtained in this titration is shown in Fig. 14.6 (*c*). In this case, the concentration of any ion does not remain constant throughout. Initially the solution of a moderately weak acid has low conductance which is further decreased by adding the alkali solution. Though sodium acetate formed here has high conducting power yet there is a fall in conductance. This is due to the repressing nature of the acetate ion *i.e.*, due to common ion effect, dissociation of acetic acid is checked. On further addition of alkali, the amount of acetate ion increases regularly as it is released from the acetic acid, until the equivalence point is reached. After the equivalence point, the conductance increases more because of the excess of OH^- ion and the curve resembles Fig. 14.6 (*a*) in its second part.

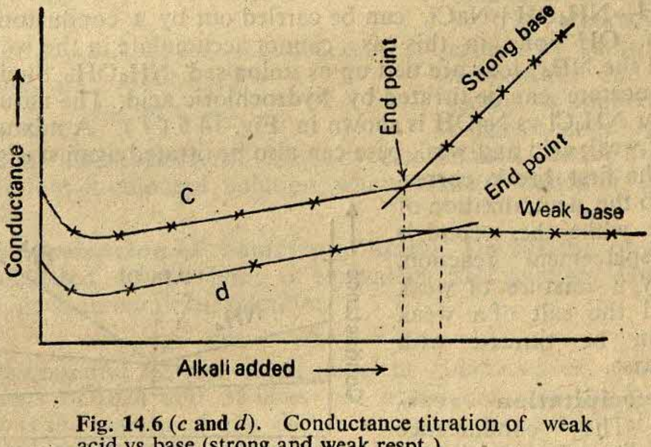


Fig. 14.6 (*c* **and** *d*). Conductance titration of weak acid vs base (strong and weak respt.).

(*d*) **Weak acid** vs **weak base.** The complete titration-curve is shown in Fig. 14.6 (*d*). The portion before the equivalence point is similar to 14.6 (*c*) due to the reasons given above. After the equivalence point, the conductance remains almost constant. As the free base is a weak electrolyte. The end point in this case is sharp.

(*e*) **Mixture of strong acid and weak acid** vs **base.** The important feature of conductometric titration is that a mixture of a strong and a weak acid can be analysed in single titrations. For this type of titration, we get two equivalence-points. The first is due to the neutralization of strong acid and second one is due to the neutralization of weak acid. The first point gives the volume of alkali for strong acid and the difference between the second and first gives the volume of alkali used for weak acid. The nature of curve is as shown in Fig. 14.6 (*e*).

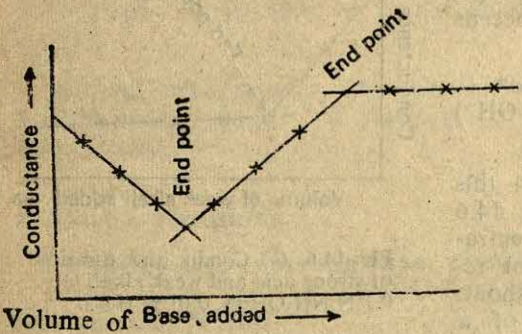


Fig. 14.6 (*e*). Conductance titration of mixture of strong and weak acid vs base.

(*f*) **Strong and weak base** vs **acid.** This can be done in the same manner as the mixture of acids. The process in this case is just reverse as the strong base is neutralized first. The acid used is strong, and very dilute or of intermediate strength. The curve obtained is of similar nature as in Fig. 14.6 (*e*).

(*g*) **Displacement reactions.** A reaction of the type $NH_4Cl + NaOH \rightarrow NH_4OH + NaCl$, can be carried out by a conductometric titration. OH^- ions, in this case. cannot accumulate in the solution until all the NH_4^+ ions are tied up as unionised NH_4OH. Similarly, sodium acetate can be titrated by hydrochloric acid. The nature of curve for NH_4Cl vs NaOH is shown in Fig. 14.6 (*f*). A mixture of a salt of weak acid and weak base can also be titrated against a strong base. The first break corresponds to the neutralization of the base while the second is for displacement reaction. Similarly, a mixture of weak acid and the salt of a weak base can be titrated with strong base.

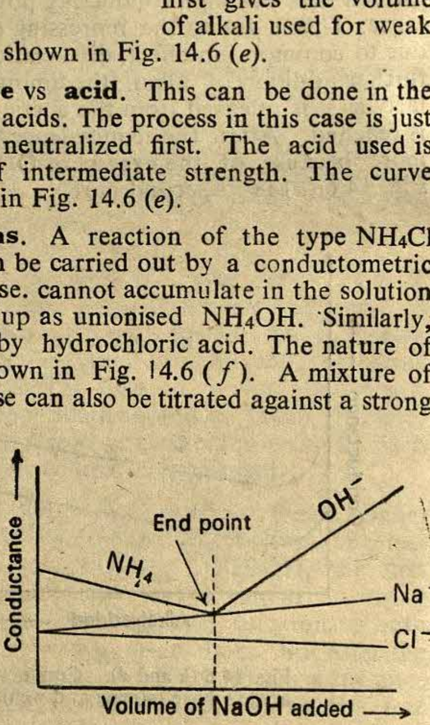


Fig. 14.6 (*f*). Conductometric titration of NH_4Cl by NaOH.

(*h*) **Precipitation reactions.** The conductance method is also applied to determine the equivalence point in precipitation titrations. The accuracy is increased by working with fairly dilute solutions in the presence of a relatively large amount of alcohol. Alcohol reduces the solubility of the precipitate and also decreases the absorption.

If KCl is titrated against $AgNO_3$, KCl is replaced by an equivalent amount of KNO_3, as shown below:

$$(K^+ + Cl^-) + (Ag^+ + NO_3^-) = AgCl + K^+ + NO_3^-$$

So, the conductance in early stages remains almost constant. After the equivalence point, there is sharp increase in conductance and we get a curve as shown in Fig. 14.6 (*g*).

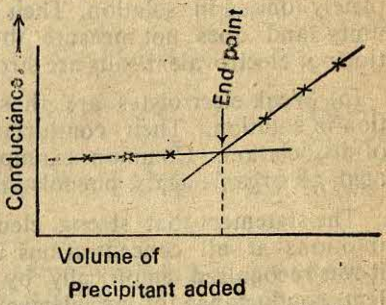


Fig. 14.6 (*g*). Conductance titration of precipitation reaction.

Similarly titrations between Ag_2SO_4 and $BaCl_2$, $MgSO_4$ and $AgNO_3$, etc., are carried out. In case of Ag_2SO_4 and $BaCl_2$, two substances are precipitated simultaneously. The conductance falls to a very low value at the equivalence point and we get a curve as shown in Fig. 14.6 (*h*). Magnesium and other sulphates can be titrated by $Ba(OH_2)$ in a similar way.

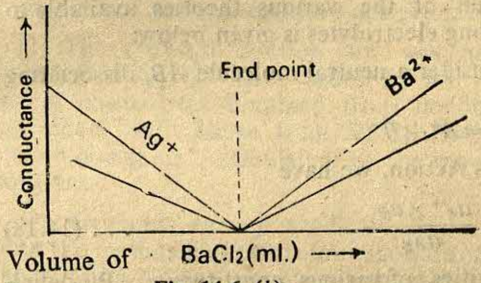


Fig. 14.6. (*h*).

The method of conductometric titration is potentially useful in any reaction where the ionic content is markedly less at the equivalence point than either before or after it. The accuracy is increased by controlling the temperature and the correction is applied for the volume change during the titration. Conductometric methods can be used for the analysis of very dilute or coloured solution where ordinary indicators give poor results.

Determination of basicity of acids. The basicity of acids can be calculated on the basis of equivalent conductances. Ostwald in 1887, gave an empirical relation:

$$\Lambda_{1024} - \Lambda_{32} = 11b$$

where Λ_{1024} and Λ_{32} are the equivalent conductances of the salt at dilutions of 1024 and 32 litres per equivalent respectively at 25°C and b is the basicity of the acid. Of course, the method fails in case of very weak acids whose salts are considerably hydrolysed in solution.

14.9. THEORIES OF STRONG ELECTROLYTES

Electrolytes, on the basis of their tendency to ionise, can be classified into two types:

(*a*) Strong electrolytes; and

(*b*) Weak electrolytes.

(*a*) Strong electrolytes are those which are largely or almost completely ionised in solution. Their conductance ratio Λ/Λ_0 approaches unity and does not measure the true degree of dissociation. Solutions of electrovalent salts are strong electrolytes.

(*b*) Weak electrolytes are those which undergo very little ionisation in solution. Their conductance ratio is a measure of the degree of dissociation. Common examples of weak electrolytes are acetic acid, all organic acids, phenols and carbonic acid.

The statement that strong electrolytes are completely dissociated into ions at all concentrations is an over-simplification. However, it was recognised empirically by Kohlrausch by plotting the equivalent conductance of an electrolyte against the square root of the concentration (*see* Fig. 14.5) that those electrolytes which lead to essentially linear plots are strong electrolytes, while those which seem to approach the dilute solution limit almost tangentially are classed as weak electrolytes.

A brief qualitative account of the various theories available to explain the behaviour of strong electrolytes is given below:

Arrhenius theory. Consider a neutral molecule *AB*, dissociating at equilibrium as:

$$AB \rightleftharpoons A^+ + B^-$$

Applying the Law of Mass Action, we have

$$K_a = \frac{a_{A^+} \times a_{B^-}}{a_{AB}} \qquad \ldots (14.18)$$

where *a* terms denote activities of various constituents. By definition,

$$a = c \times f \qquad \ldots (14.19)$$

where *c* is concentration and *f* is activity co-efficient. The activity coefficient cannot be neglected in concentrated solutions. However, in dilute solutions, activity may be taken to be equal to concentration (the activity co-efficient is equal to unity). Equation (14.16) can be written as:

$$K_c = \frac{c_{A^+} \times c_{B^-}}{c_{AB}} \qquad \ldots (14.20)$$

Let the fraction α of the salt be dissociated in a solution of concentration *c*. Therefore, at equilibrium

$$c_{AB} = c(1-\alpha) \text{ and } c_{A^+} = c_{B^-} = c\alpha$$

On substituting this in equation (14.18), we get

$$K_c = \frac{c\alpha^2}{(1-\alpha)} \qquad \ldots (14.21)$$

Since the conductance ratio equals the degree of dissociation, *i.e.*,

$$\alpha = \frac{\Lambda}{\Lambda_0}$$

Equation (14.19) can be written as:

$$K_c = \frac{\Lambda^2 c}{\Lambda_0(\Lambda_0 - \Lambda)} \qquad \ldots (14.22)$$

or

$$K_c = \frac{\Lambda^2}{V\Lambda_0(\Lambda_0 - \Lambda)} \qquad \ldots (14.23)$$

where $V\left(=\frac{1}{c}\right)$ is the dilution. Equation (14.23) is a well known equation of Ostwald dilution law.

Arrhenius assumed that the ionic speeds were independent of the concentration of the solution. He ascribed the change of equivalent conductance with concentration to the change in the number of ions produced from one equivalent of the electrolyte. Arrhenius theory led to a great advance in our knowledge of the molecular behaviour of solutions of electrolytes. This theory met with some serious difficulties when it was tested with strong electrolytes. Some anomalies of Arrhenius theory are given below:

(1) The Ostwald dilution law was not obeyed by moderately strong electrolytes. The values for the degree of dissociation α of strong electrolytes obtained from conductance ratios were not in agreement with those from Van't Hoff *i* factors and the "dissociation constants" calculated by the mass-action law were far from constant.

(2) Arrhenius theory predicted that the transport numbers of both the cations and the anions should increase equally with increasing dilution. This, however, provided no explanation why their relative mobilities should vary.

(3) Though one of the interesting feature of the Arrhenius theory is that it attributes the dissociation process to the solution of the electrolyte, it however, proceeds to ignore the role of the solvent and treats the solvent as if it were an inert medium.

(4) The absorption spectra of dilute solutions of strong electrolytes revealed no evidence for undissociated molecules.

The electronic theory of valency and the results of X-ray study of crystals of salts classed as strong electrolytes lead us to believe that these are completely ionised at moderate concentrations. Hence the variation of equivalent conductance cannot be ascribed to a change in the number of ions as this is constant for 1 gm equivalent of the electrolyte at all concentrations.

The falling off in the equivalent conductance must then be due to a decrease in the ionic velocity with increasing concentration.

This is the basis of the interionic attraction theory, the quantitative treatment of which is mainly due to the work of P. Debye and E. Huckel (1932) and ol L. Onsager (1926).

The theory is based on the assumption that strong electrolytes are completely dissociated into ions. The observed deviations from ideal behaviour are ascribed to electrical interactions between the ions. This comprises two parts: (*a*) ionic atmosphere, and (*b*) asymmetry or relaxation effect.

(*a*) **Ionic atmosphere**. In any electrolytic solution, each ion is surrounded by oppositely charged ions. Consider a solution of sodium chloride. A central positive charge (Na^+) attracts the electron clouds of oppositely charged ions (Cl^-) in its vicinity. Each Na^+ will be surrounded by Cl^- ions. The central Na^+ will have an ion atmosphere of oppositely charged ions. This gives rise to a decrease in the velocity of the ion. See Fig. 14.7 (*a*) Picture of the cation with symmetrical ionic atmosphere about it, in the absence of an electric field, and (*b*) an instantaneous picture of a cation and its ionic atmosphere in an electric field.

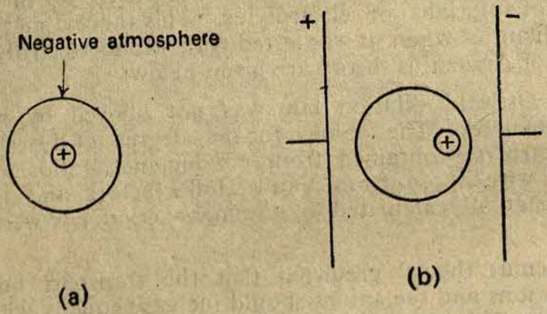


Fig. 14.7. Origin of the asymmetry effect.

(*c*) **Asymmetry or relaxation effect**. When a potential is applied across a solution, cations will move towards the cathode and the anions towards the anode. The oppositely charged ionic atmospheres take sometimes to readjust themselves. Since the ion and its atmosphere have opposite charges, there is an electrostatic attraction between them. This results in slowing down the motion of the ion. This effect on the speed of the ion is known as the asymmetry or relaxation effect. It arises due to the lack of asymmetry in the atmosphere of a moving ion resulting from the slowness of readjustment of the ionic atmosphere. In addition, the factor which results in a retardation of the ionic motion, is the tendency of the applied E.M.F. to move the oppositely charged ionic atmosphere with its associated molecules of water of hydration in a direction opposite to that in which the central ion is moving. This results in an additional retarding influence equivalent to an increase in viscosity of the solvent on the moving ion. The atmosphere thus tends to drag the ion with it, and this is referred to as the electrostatic effect.

The magnitudes of these effects have been taken into consideration in the derivation of Onsager equation for a univalent strong electrolyte that is, an electrolyte which gives two univalent ions in solution. The Onsager equation is

$$\Lambda=\Lambda_o-\left[\frac{82.4}{(DT)^{1/2}\eta}+\frac{8.20\times10^5}{(DT)^{3/2}}\cdot\Lambda_o\right]\sqrt{c} \quad \ldots (14.24)$$

where D is the dielectric constant of the medium, T is the temperature and η the coefficient of viscosity of the medium. It can easily be shown that the Debye-Hückel approximation becomes exact in the limit of zero electrolyte concentration. The Debye-Huckel theory becomes inaccurate for concentration in excess of $10^{-3}M$.

In a more general form of equation (14.24), we have

$$\Lambda=\Lambda_o-(A+B\Lambda_o)\sqrt{c} \quad \ldots (14.25)$$

where A and B are constants for a given solvent and depend on the temperature. Plot of Λ against square root of the concentration (Fig. 14.8) show straight line behaviour at low concentrations. In recent years various attempts have been made to explain the behaviour of strong electrolyte.

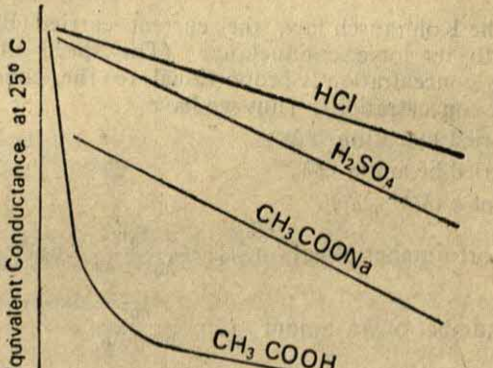


Fig. 14.8. Equivalent conductances of strong and weak electrolytes (Test of Onsager equation).

Various attempts have been made to apply Debye-Hückel theory to concentrated solution, with certain modifications. These modifications, however, do result in some improvements, but do less well in predicting the properties of real electrolyte solutions. This suggests that a more refined model of the electrolyte solution is needed. For example in Debye-Huckel model, we have not taken into account van der Waals type interactions between the ion and the solvent. Clearly, the statistical molecular theory of electrolyte solutions needs considerable development before it can be treated to give a realistic and quantitative description of the influence of ions on the structure of water and on the thermodynamic properties of the solution for the entire range of composition.

14.10. TRANSFERENCE NUMBERS

We have seen that the different types of ions move with different speeds under the same potential gradient. It, therefore, follows that the cations and the anions carry different amounts of electricity during the electrolysis. This current carried by individual ions depend upon its velocity, and the total current is constituted by the movement of cations and anions.

"*The fraction of the current carried by a given ionic species in the solution is called the Transport Number or Hittorf's number or transference number of the ion and designated by the symbols.*" In the simplest case of a single electrolyte yielding two ions, denoted by the suffixes + and −, the symbols for transport number are t_+ and t_- respectively.

According the Kohlrausch law, the current carried by an ion is proportional to its ionic conductance. (The speed of an ion in a solution at any concentration is proportional to the conductance of the ion at that concentration). Thus we have

Current carried by cation $\propto \lambda_0^+$

Current carried be anion $\propto \lambda_0^-$

Total current $\propto (\lambda_0^+ + \lambda_0^-)$

$\therefore$ Transport number of cation, $t_+ = \dfrac{\lambda_0^+}{\lambda_0^+ + \lambda^{0-}}$ and

Transport number of an anion; $t_- = \dfrac{\lambda_0^-}{\lambda_0^+ + \lambda_0^-}$

The transport number of the ions can be measured by finding the change in concentration round the electrodes. To illustrate this, let us consider the electrolysis cell shown in Fig. 14.9. Further, let the solutions be divided into three compartments by means of imaginary partitions *ab* and *cd*. In the diagram, ⊖ represents anion and ⊕ represents cation. Before electrolysis, the position of the ions is shown by the line I, where every anion is associated with a cation.

Case I. Let the cation and the anion move with the same speed and say two anions have crossed the partition towards the anode; then two cations will have crossed in the opposite direction towards the cathode. This is shown in line II. As a result of this, excess ions in the two compartments near the anode and the cathode are discharged as shown in line III. Here the cathode becomes dilute to the same extent.

Case II. Let the anion moves with twice the speed of the cation and further let two cations reach the cathode. Then four anions will cross to the anode compartment. The state now is as in *IV.* The excess ions near the anode and the cathode compartment are liberated. The state of the solution is as shown in *V.* The fall in the amount of electrolyte near the anode will be $(5-3)=2$ and that near the cathode will be $(5-1)=4$. These fall in concentration near the two electrodes are proportional to the speed of the ions leaving that compartment *i.e.*,

$$\frac{\text{Fall near the anode}}{\text{Fall near the cathode}}=\frac{\text{Speed of cation}}{\text{Speed of anion}} \qquad \ldots (14.24)$$

Let t_- is the fraction of the current carried by the anion; then the fraction $1-t_-$ must be carried by the cation. Since the amounts of electricity carried are proportional to the speed of the ions, we have:

$$\frac{\text{Loss at anode}}{\text{Loss at cathode}}=\frac{1-t_-}{t_-}$$

If u is the speed of the anion and v is the speed of the cation, then we have

$$\frac{t_-}{t_+}=\frac{t_-}{1-t_-}=\frac{\text{Loss at cathode}}{\text{Loss at anode}}=\frac{u}{v} \qquad \ldots (14.25)$$

14.10. METHODS FOR THE DETERMINATION OF TRANSPORT NUMBERS

There are two methods for the determination of transport numbers: (*i*) Hittorf method and (*ii*) Moving boundary method.

(*i*) **Hittorf method**. Several types of apparatus have been devised for the determination of transference numbers by the Hittorf method, the one which is most commonly used is shown in Fig. 14.10.

The apparatus is filled with the experimental solution whose weight concentration is known. The electrodes are connected in series with a silver voltameter. The solution is electrolysed sufficiently long to give an appreciable change in concentration round the electrodes. However, too long a time must not be used otherwise the results will be vitiated by diffusion etc. A current of 0.01 ampere is passed for two to three hours. The solution from each compartment is analysed at the end of the experiment. There should be no change in concentration in the middle compartment. The quantity of electricity passed through the cell is obtained from the increase in weight of the

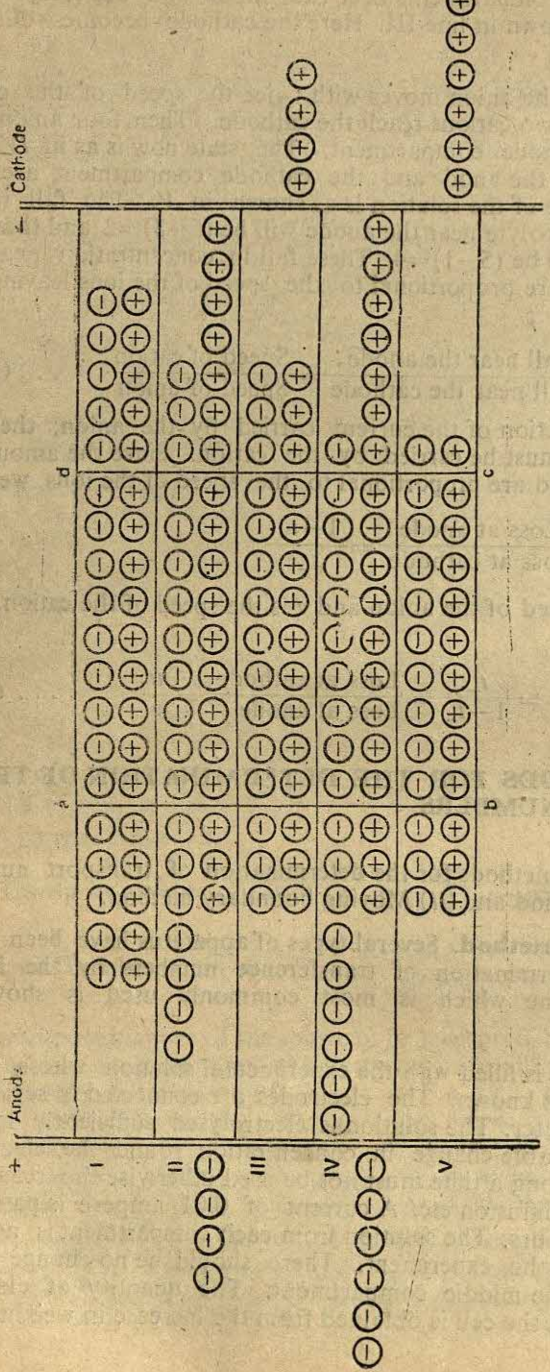


Fig. 14.9. Migration of ions.

cathode in the coulometer. Let a grams of the anode solution was found to contain b grams of the electrolyte on analysis. Then the solution contained $a-b$ grams of water. On analysis of the original solution, let d grams be the amount of electrolyte associated with the same amount of water. The decrease of electrolyte concentration in the anode compartment will be $d-b$ grams or $(d-b)/e$ equivalents where e is the equivalent weight of the experimental substance. If c is the number of equivalents of the material deposited in the coulometer during the electrolysis, the transport number of the cation (t_+) is given by:

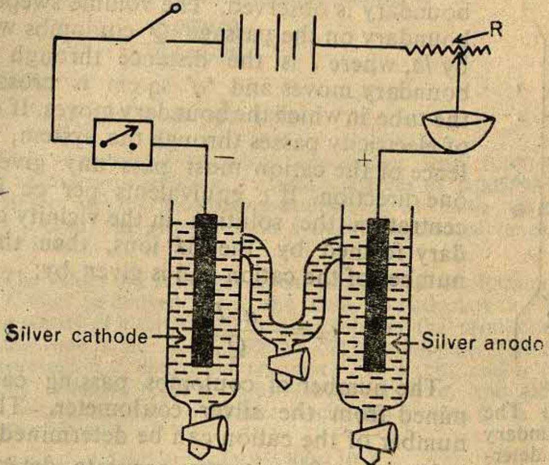


Fig. 14.10. Hittorf Method.

$$t_+ = \frac{d-b}{c.e} \qquad \ldots (14.26)$$

The transport number of anion (t_-) is given by $(1-t_+)$.

(*ii*) **Moving boundary method**. The moving boundary method, on account of its relative simplicity and accuracy, has been used for precision measurements. The apparatus employed is shown in Fig. 14.11. It consists of a tube mounted vertically. *A* solution of electrolyte to be investigated *MA e.g.*, potassium chloride, is placed in between layers of solutions of two other electrolytes *M'A* and *MA'* each of which has an ion in common with *MA e.g.*, lithium chloride (*M'A*) and potassium acetate (*MA'*). The solutions *M'A* and *MA'* act as indicators. The sharp boundaries are formed at *a* and *b* as shown. In order that the boundaries may remain sharp during the passage of the current, the speed of the indicator ion *M'* should be less than that of *M* and that speed of *A'* should be less

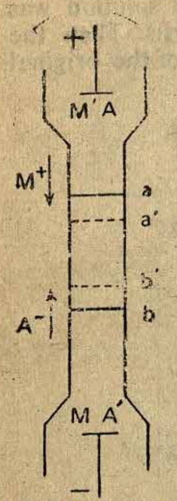


Fig. 14.11. The moving boundary method of determining transport number.

than that of the *A* ions. Under the influence of an electric field the boundary *a* moves to *a*′ and *b* moves to *b*′. The distances *aa*′ and *bb*′ depend on the speed of the ions. In actual practice only one boundary is observed. The volume swept out by the boundary on the passage *Q* coulombs will be given by *la*, where *l* is the distance through which the boundary moves and '*a*' sq cm is cross-section of the tube in which the boundary moves. If one faraday of electricity passes through the system, t_+ equivalence of the cation must pass any given point in one direction. If *c* equivalents per cc is the concentration the solution in the vicinity of the boundary formed by the *M* ions, then the transport number of the cation (t_+) is given by:

$$t_+ = \frac{l.a.\ F.c}{Q} \qquad \ldots (14.27)$$

The number of coulombs passing can be determined from the silver coulometer. The transport number of the cation can be determined.

However, for a more accurate determination of the transport number, a correction must be applied for the change in volume occurring as a result of reactions at the electrodes.

Problem 14.5. Determine the transport numbers of the ions of an exactly 0.20 molal solution of copper sulphate, the cell was filled with the solution and electrolysed between copper electrodes for some time. The cathode solution from cell was found to weight 36.4340 g. and to contain 0.4415 g. of copper. Further the cathode in coulometer showed an increase in weight of 0.0405 g due to deposited silver.

Solution. The 36.4340 g. of final cathode solution contained 0.4415 g. of copper, which is equivalent to 1.1090 g. of $CuSO_4$.

The weight of water in this solution was, then

$$36.4340 - 1.1090 = 35.3250 \text{ g.}$$

Now, since before electrolysis, the solution was 0.2000 molal, each gram of water had associated with it $0.2000 \times \frac{CuSO_4}{1000}$ g. of the salt.

Hence 35.3250 g. of water had associated with them initially,

$$35.3250 \left(0.2000 \times \frac{CuSO_4}{1000} \right) = \frac{35.3250 \times 0.2000 \times 159.6}{10000}$$

$$= 1.1276 \text{ g } CuSO_4.$$

Therefore, the loss in weight of the copper sulphate in cathode compartment is equal to

$$1.1276 - 1.1090 = 0.0186 \text{ g.}$$

or

$$2 \times 0.0186/159.60 = 0.000233 \text{ equivalent}$$

The total current passed through the cell is given by 0.0405 grams of silver.

or

$$0.0405/107.87 = 0.000375 \text{ equivalent.}$$

Consequently, the loss in copper sulphate due to deposition of copper on cathode should have been this number of equivalents. But the actual loss was only 0.000233 equivalent and hence the difference 0.000375 − 0.000233 = 0.000142 equivalent, must have migrated into this compartment. As the ion that migrates toward the cathode is Cu^{++}, this number of equivalents must have been transported by this ion and therefore, the transport number is

$$t_{Cu^{++}}=\frac{0.000142}{0.000375}=0.379$$

while that of SO_4^{--} is

$$t_{SO_4^{--}}=(1-0.379)=0.621.$$

Problem 14.6. In a moving boundary experiment with 0.100 N KCl using 0.065 N LiCl as indicator solution, a constant current of 0.005893 ampere was passed for 2180 sec. and the boundary was observed to move through 5.60 cm. in a tube of 0.1142 sq. cm. cross-section. Calculate the transference numbers of the K^+ and Cl^- ions.

Solution. The values of l and a are given, while that of Faraday is known; hence Q and C must be derived from the data to calculate t_+ by equation (14.28). The quantity of electricity Q in coulombs is the product of the current in amp. and the time in sec. *i.e.*, 0.005893×2130 coulombs. The concentration C must be expressed in g. equiv. per cc., since l is in cm. and a in cm^2. The solution of KCl contains 0.100 g. equivalence per litre, and this is 10^{-4} g. equiv. per ml or per c.c. with sufficient accuracy, hence C is 10^{-4} and by equation (14.28)

$$t_+=\frac{5.60\times0.1142\times965500\times10^{-4}}{0.005893\times2130}=0.492$$

The transference number of the K^+ ion is thus 0.492 and that of Cl^- ion is = (1 − 0.492) = 0.508.

Results of Transport Number Determinations

Some of the results of transport number measurements are presented in Table 14.2.

TABLE 14.2.

Transport numbers of cations in water solutions at 25°C

Solution normality	*$AgNO_3$*	*LiCl*	*NaCl*	*KNO_3*	*$BaCl_2$*	*K_2SO_4*
0.01N	0.4648	0.3289	0.3918	0.5084	0.440	0.4829
0.05N	0.4664	0.3211	0.3876	0.5093	0.4317	0.4870
0.100N	0.4682	0.3168	0.3844	0.5103	0.4253	0.4890
0.20N	—	0.3112	0.3821	0.5120	0.4162	0.4910
0.50N	—	0.300	—	—	0.3986	0.4909
1 0N	—	0.287	—	—	0.3792	—

The variation of the transport numbers with the concentration of the electrolyte was proposed by Onsager *i.e.*,

$$t=t_o-A\sqrt{C} \qquad \ldots (14.28)$$

where t and t_o are the transference numbers of a given ion in a solution of concentration C and that extrapolated to infinite dilution respectively. A is a constant. This equation is valid only for dilute solutions.

14.11. ABNORMAL TRANSFERENCE NUMBERS

Since the ions in solution are hydrated, hence the transport numbers are not those of 'bare ions' but of solvated ions. It has been found that solution of cadmium iodide exhibits a marked deviation in transport number with concentration as shown in Table 14.3.

TABLE 14.3.

Conc	0.0005	0.01	0.02	0.05	0.1	0.2	0.5N
t_+	0.445	0.444	0.442	0.396	0.296	0.127	0.003

The transport number of cadmium apparently becomes negative at concentrations greater than 0.5N. The negative value of transport number in concentrated solutions indicates that in cadmium iodide, cadmium is being carried in a direction opposite to that in which the positive electricity moves through the solution. The possible explanation for this abnormal behaviour may be due to the following reactions in a concentrated solution.

$$CdI_2 + 2I^- \rightleftharpoons CdI_4^{2-}$$

i.e., in a concentrated solution, appreciable amounts of cadmium are present as anions CdI_4^{2-}.

In a dilute solution, on the other hand, we have:

$$CdI_2 \rightleftharpoons Cd^{2+} + 2I^-$$

Thus, if equal amounts of electricity are carried in opposite direction by Cd^{2+} and CdI_4^{2-} ions, the transport number of cadmium will appear to be zero. Further if the speed of CdI_4^{2-} be greater than that of Cd^{2+}, the apparent cation transport number will appear to be negative.

PROBLEMS

1. Define the term *electrolysis*. State and explain Faraday's Laws of electrolysis. Bring out clearly the theoretical importance of these laws.

2. Explain the terms : *Conductance*, *specific conductance*, *equivalent conductance* and *molecular conductance*. Derive a relation between specific conductance and equivalent conductance of a solution.

3. A conductance cell with a constant of 2.485 cm^{-1} is filled with a KCl solution for which $\Lambda = 141.3$ ohm^{-1} cm^2 at 25°C. If the specific conductance of the water is 1.0×10^{-6} ohm^{-1}, what was the resistance of the solution?

Ans. 2150 ohms.

4. Which of the following units can be used for the cell constant?

(*a*) cm^{-1}

(*b*) $ohm^{-1}\ cm^{-1}$

(*c*) cm

(*d*) ohm^{-1} cm

Ans. cm^{-1}

5. A conductivity cell has a resistance of 250 ohms when filled with 0.02 M KCl at 25°C and one of 10^5 ohms when filled with 6×10^{-5} M ammonium hydroxide solution. The specific conductivity of 0.62 M KCl is 0.00277 ohm^{-1} cm^{-1} and the equivalent conductivities for NH_4^+ and OH^- are 73.4 and 198.0 respectively. Calculate the cell constant and degree of dissociation of ammonium hydroxide in the 6×10^{-5} M solution

Ans. $k = 0.692$; $\alpha = 0.423$

6. Discuss clearly the limitations of the Arrhenius theory. How are these accounted for on the basis of the theory of strong electrolytes by Debye and Huckel.

7. The specific conductance of a saturated solution of silver chloride at 25°C after subtracting the specific conductance of water is 2.28×10^{-6} ohm^{-1}. Calculate the solubility of silver chloride at this temperature ($\Lambda_0 AgCl = 138.3$ ohm^{-1}).

Ans. 2.358×10^{-3} gm. per litre.

8. The specific conductance at 25°C of a saturated aqueous solution of $SrSO_4$ is 1.482×10^{-4}, while that of the H_2O used is 1.5×10^{-6} ohm^{-1} cm^{-1}. Determine at 25°C the solubility in grams per litre of $SrSO_4$ in water.

Ans. 0.0967 g/litre.

9. State and explain Kohlrausch's Law of independent migration of ions. How does it help in determining the equivalent conductivity at infinite dilution of weak electrolytes.

10. What is meant by transport number of an ion? Describe a suitable method for the determination of the transport number of Ag^+ and NO_3^- ions in a solution of $AgNO_3$.

11. A $AgNO_3$ solution containing 0.00739 gm of $AgNO_3$ per gm of H_2O is electrolysed between silver electrodes. During the experiment, 0.078 gm of Ag is deposited at the cathode. At the end of the experiment, the anode portion contains 23.14 gm of H_2O and 0.236 gm of $AgNO_3$. What are the transport numbers of Ag^+ and NO_3^- ions?

Ans. $t_{Ag^+} = 0.47$

12. A solution of lithium chloride containing 0.86356 gm of salt per 100 g of water was electrolysed using a Ag anode and AgCl cathode. At the end of the run, 1.375588 gm of silver had been deposited in a coulometer. The anode solution, weighing 124.894 g, contained 0.72899 gm of salt per 100 g of water and the cathode solution weighing 123.456 g contained 1.00032 g of salt per 100 g of water. Calculate the transference number of lithium ion from the data for each solution.

Ans. Anode = 0.3109
Cathode = 0.3109

13. The transference numbers of the ions in 1.00 N KCl were determined by the moving boundary method using 0.80 N $BaCl_2$ as the following solution. With a current of 0.0142 amp., the time required for the boundary to sweep through a value of 0.1205 c.c. was 1675 sec. What are the transport numbers of K^+ and Cl^- ions?

Ans. $t_+ = 0.40$
$t_- = 0.60$

14. A solution of $AgNO_3$ containing 0.0074 g per gram of water was electrolysed using silver electrodes. During the experiment, 0.0785 g of Ag was deposited in a silver voltameter. At the end of electrolysis, 25 g of anode solution

contained 0.2553 g of $AgNO_3$. Calculate the transport number of NO_3^- ion. (Atomic weight of Ag=108 ; N=14, O=16).

Ans. 0.569

15. Give suitable explanations for the following:

(*a*) The resistance of a metal increases and that of an electrolyte decreases on raising the temperature.

(*b*) When the concentration of an electrolyte in a solution is increased, its conductivity increases and its equivalent conductance decreases.

(*c*) Equivalent conductances of hydrogen and hydroxyl ions are much greater than those of other ionic species.

(*d*) Experimentally measured degree of dissociation of any strong electrolyte is less than one.

16. In a transport number determination experiment, it is essential to avoid gas formation during electrolysis. Explain.

17. Derive a relationship between ionic mobilities and equivalent ionic conductances of ionic species in solutions. How is the degree of dissociation of acetic acid determined ?

Chapter 15

IONIC EQUILIBRIA

15.1. THE OSTWALD'S DILUTION LAW

The law of mass action can also be applied to equilibrium involving ions in the same manner as was done in chemical equilibrium. The application of the Law of Mass Action to weak electrolytes was first attempted by Ostwald (1888) and the equation deduced by him is known as *Ostwald's Dilution Law*.

Consider a binary electrolyte AB which dissociates into charged ions A^+ and B^- according to the equation

$$AB \rightleftharpoons A^+ + B^- \qquad \ldots (15.1)$$

If C moles/litre is the concentration of the electrolyte and α is its degrees of dissociation, then the various concentration terms at equilibrium are given by

$$C_{AB} = C(1-\alpha),\ C_{A^+} = C\alpha \text{ and } C_{B^-} = C\alpha$$

Applying the Law of Mass Action,

$$K_C = \frac{C_{A^+}.C_{B^-}}{C_{AB}} = \frac{C\alpha.C\alpha}{C(1-\alpha)}$$

or

$$K_C = \frac{\alpha^2 C}{(1-\alpha)} \qquad \ldots (15.2)$$

The equilibrium constant K_C for reactions involving ions is called the ionisation constant or dissociation constant of the electrolyte and, like other equilibrium, is a constant only at constant temperature.

If 1 gm molecule of the electrolyte is dissolved in V litres of the solution, then

$V = 1/C$ (V is called the dilution for the solution)

Therefore, equation (15.2) can also be written as

$$K_C = \frac{\alpha^2}{(1-\alpha)V} \qquad \ldots (15.3)$$

Equation (15.3) which represents the variation of degree of dissociation with dilution is known as the Ostwald's Dilution Law.

In case of weak electrolytes, the value of α is negligibly small as compared to unity so that $1-\alpha \approx 1$.

Therefore, equation (15.3) becomes

$$\frac{\alpha^2}{V}=K_C \text{ cr } \alpha=\sqrt{K_C.V}$$

In other words, the degree of dissociation for weak electrolytes is directly proportional to the square root of dilution.

In case of strong electrolytes, α is quite large and is not negligible in comparison to unity. The equation becomes a quadratic one.

$$\frac{\alpha^2}{(1-\alpha)V}=K_C \text{ or } \alpha^2=K_CV-\alpha K_CV$$

This can also be written as

$$\alpha^2+\alpha K_CV-K_CV=0$$

from which α follows as

$$\alpha=\frac{-K_CV\pm\sqrt{K_C{}^2V^2+4K_CV}}{2}$$

Experimental verification of the dilution law. The Ostwald Dilution Law can be experimentally tested by substituting the degree of dissociation (α) of a binary electrolyte at different dilutions (V) in the expression

$$K_C=\frac{\alpha^2}{(1-\alpha)V}$$

and thus calculating the value of K_C. If K_C comes out to be constant, the law is valid. It was found that the law is valid only for weak electrolytes (mainly weak acids and weak bases) in dilute solution (V is large).

The degree of dissociation α is best determined by the expression

$$\alpha=\frac{\lambda v}{\lambda\infty}$$

where λ_V is the equivalent conductivity at dilution V and λ_∞ is that at infinite dilution. λ_V and λ_∞ can be easily determined by conductivity measurements and Kohlrausch's Law of ionic mobilities respectively.

Limitations of Ostwald's dilution law. This law holds good only for weak electrolytes and fails completely in the case of strong electrolytes. The failure of the law in the case of strong electrolytes is attributed to the following factors :

(*i*) Ostwald's Dilution Law is based on Arrhenius Theory of weak electrolytic dissociation according to which all electrolytes are partially dissociated into charged particles and dissociation is complete only at infinite dilution. This is true for weak electrolytes and not for strong electrolytes. Strong electrolytes are completely dissociated at all dilutions *i.e.*, $\alpha=1$.

(*ii*) When applying Law of Mass Action to the equilibrium involving ions, concentration terms of all the reacting species were taken. As a result of the presence of ions in the solution, there are electrostatic forces between charged particles. These interionic forces, although small in weak electrolytes, are quite significant in case of strong electrolytes. Hence, instead of using concentration terms, activities should be used. Thus, for the equilibrium

$$AB \rightleftharpoons A^+ + B^-$$

Law of Mass Action is written in the form

$$K_a = \frac{a_{A^+} . a_{B^-}}{a_{AB}} \qquad \ldots (15.4)$$

where a_{A^+}, a_{B^-} and a_{AB} are the activities of the cation, anion and the undissociated electrolyte respectively. Since the activity is related to the concentration by the following equation:

Activity (a) = Concentration (C) × Activity Coefficient (f)

$$K_a = \frac{C_{A^+} . C_{B^-}}{C_{AB}} \times \frac{f_{A^+} . f_{B^-}}{f_{AB}}$$

The activity coefficient varies with concentration. As the concentration decreases, $f \rightarrow 1$. Only under extreme dilutions, Law of Mass Action is applicable in terms of concentrations.

15.2. CONCEPTS OF ACIDS AND BASES

The nature and the concept of acids and bases has been a matter of speculation since the time of Robert Boyle in the seventeenth century. The word 'acid' comes from the Latin word acidus, meaning sour. The first descriptive term for a substance opposite in properties to an acid was a word alkali; a word derived from the Arabic words al-qili, meaning the ashes of a plant. The first established characteristic of an alkali, was to destroy the action of an acid. Lavoisier in 1787 postulated that acids were binary compounds containing oxygen. He showed that a number of elements such as carbon, nitrogen and sulphur burned in oxygen to give compounds which acted as acids in water solution. This was popularly known as acid-oxygen theory, which remained in existence until it was recognised that acids do not necessarily contain oxygen. However, the first attempt to give a structural definition of acids and bases was made by Arrhenius in 1887. Arrhenius defined an acid as a substance, which gives hydrogen ions (H^+) in solution and a base as a substance, which gives hydroxyl ions (OH^-) in solution. Then the neutralisation process was simply $H^+ + OH^- = H_2O$. Although these definitions of acid and base can satisfactorily explain some of the observed phenomena in aqueous solutions, they fail to explain all observed phenomena both in aqueous and in non-aqueous solutions.

A major improvement in the classical definition of acid and basess, proposed by Arrhenius, was made by Bronsted and Lowry in 1927. They defined acids and bases in terms of proton transfer. According to them, an acid is a substance, which has a tendency to donate a proton and base is a substance, which has a tendency to accept a proton. It follows from these two new definitions of acids and bases that when an acid donates a proton, there must be some base to accept it and vice-versa. This can be illustrated by the general expression.

$$\text{Acid} \rightleftharpoons H^+ + \text{Base}$$

Thus, we see that every acid has a base corresponding to it which differs by a proton. This base is said to be the base conjugate to the acid.

Acids and Bases can either be neutral molecules or charged particles.

Bronsted also showed that a proton does not exist as H^+ in aqueous solution but as hydrated proton, H_3O^+.

$$H^+ + H_2O \rightarrow H_3O^+$$

H_3O^+ is known as the hydronium ions because of its resemblance with ammonium (NH_4^+) ion. The hydronium ion is further hydrated but for simplicity and convenience, it is taken as H_3O^+. Sometimes, it is further simplified by writing as H^+.

The difference between the classical concepts of acids and bases and the generalised concept of Bronsted and Lowry can be easily explained with several examples. Consider acetic acid as one of the examples. According to both the concepts, acetic acid is an acid. The classical concept represents the ionisation of acetic acid as

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

whereas the generalised concept represents its ionisation as

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

In the latter equation, we see that acetic acid ionizes by donating the proton to a water molecule, which acts as a base. This results in the formation of a hydronium ion and an acetate ion. In the reverse reaction, H_3O^+ is the acid because it can donate a proton to the acetate ion, the base. Thus, we see that *the reaction between an acid and a base always results in the formation of a new acid and a new base.* Since the product acid, H_3O^+ is formed when the reactant base, H_2O, accepts a proton; H_3O^+ and H_2O are said to comprise a conjugate acid-base pair. Similarly, since the product base, CH_3COO^- results when the reactant acid, CH_3COOH, donates a proton; CH_3COOH and CH_3COO^- also comprise another conjugate acid-base pair. Designating one conjugate acid-base pair in the reaction by the subscript 1 and the other pair by the subscript 2, the general expression for all types of acid-base reactions can be represented as

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1$$

$Acid_1$—$Base_1$ comprise one conjugate pair and $Acid_2$—$Base_2$ comprise the other conjugate pair.

Some typical examples of the ionization equilibrium of various acids in water are given below:

$$\begin{array}{llll}
\text{Acid}_1 & \text{Base}_2 & \text{Acid}_2 & \text{Base}_1 \\
HCl & +H_2O \rightleftharpoons & H_3O^+ + & Cl^- \\
HCOOH & +H_2O \rightleftharpoons & H_3O^+ + & HCOO^- \\
H_2CO_3 & +H_2O \rightleftharpoons & H_3O^+ + & HCO_3^- \\
HCO_3^- & +H_2O \rightleftharpoons & H_3O^+ + & CO_3^{2-} \\
HNO_3 & +H_2O \rightleftharpoons & H_3O^+ + & NO_3^- \\
NH^+_4 & +H_2O \rightleftharpoons & H_3O^+ + & NH_3 \\
H_2O & +NH_3 \rightleftharpoons & NH^+_4 + & OH^-
\end{array}$$

In the above examples, it can be noticed that water behaves both as an acid and a base depending on the conditions of the reaction. Similar is the behaviour of HCO_3^- and alcohol. These types of substances which can act both as an acid and a base are said to be *amphoteric*.

Relationship between the strengths of the acids and their conjugate bases. The Bronsted-Lowry definition suggests that the strength of an acid is determined by its tendency to lose protons and the strength of a base is determined by its tendency to accept protons. Thus a strong acid will have a large tendency to donate a proton to another molecule while a strong base will have a large affinity for protons. Hydrochloric acid is said to be stronger than the acetic acid because HCl has a larger tendency to donate a proton to water molecule and the equilibrium

$$\begin{array}{llll}
\text{Acid}_1 & \text{Base}_2 & \text{Acid}_2 & \text{Base}_1 \\
HCl & +H_2O \rightleftharpoons & H_3O^+ + & Cl^- \\
\text{(Stronger)} & \text{(Stronger)} & \text{(Weaker)} & \text{(Weaker)}
\end{array}$$

shift considerably to the right and the reverse reaction, which represents the transfer of a proton from the acid H_3O^+ to the base, occurs to a very small extent only. Thus Cl^- is a weak base.

But in the case of acetic acid, the equilibrium

$$\begin{array}{lllll}
\text{Acid}_1 & \text{Base}_2 & & \text{Acid}_2 & & \text{Base}_1 \\
CH_3COOH + & H_2O & \rightleftharpoons & H_3O^+ & + & CH_3COO^- \\
\text{(Weaker)} & \text{(Weaker)} & & \text{(Stronger)} & & \text{(Stronger)}
\end{array}$$

is more on the left side than on the right side because CH_3COOH is a weak acid and its conjugate base, CH_3COO^- is strong.

In general it can be said that *the stronger an acid, the weaker is its conjugate base and vice-versa.*

In order to compare the strengths of various acids, it is necessary to measure their tendencies of transferring a proton to the same common solvent. (Measurements are done in terms of dissociation constants). Thus, by measuring the ability of various acids to transfer a proton to glacial acetic acid, we can rank them in the following order of decreasing strength:

$$HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$$

(Although acetic acid is a weak acid but still it has a tendency of accepting a proton only from a very strong acid.) The ionization of a strong acid in acetic acid takes place as shown below:

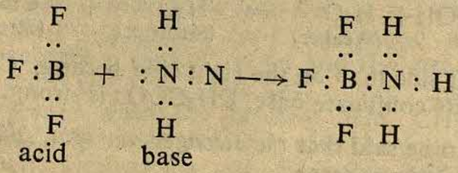
$$\underset{\text{Acid}_1}{HA} + \underset{\text{Base}_2}{CH_3COOH} \rightleftharpoons \underset{\text{Acid}_2}{CH_3COOH^+_2} + \underset{\text{Base}_1}{A^-}$$

In the case of weak acids, such as acetic acid, strength can be measured in water, but in the case of strong acids, it is not possible. This is due to the fact that all strong acids are completely ionized in water and the product H_3O^+ formed is the strongest acid that can exist in water. Thus in water, all strong acids appear to be equally strong and their strengths cannot be distinguished. This effect is known as the "levelling effect" of the solvent and can be overcome by using a weaker base than water. It is due to this reason that strength of strong acids as listed above is measured in glacial acetic acid as the solvent. In acetic acid, even the strong acids are slightly ionized.

Lewis acid-base concept. In 1923, G.N. Lewis proposed a new concept of acids and bases in terms of sharing of an electrons pair. According to this theory, *a base is a substance which donates a pair of electrons in covalent bonding and an acid is a substance which accepts the pair of electrons from the donor substance, the base.* The acid is known as the *electrophile* and the base is known as the *nucleophile*. Thus in the neutralization process, a covalent bond is formed in which both the electrons of the shared pair are provided by the base. This theory also leads to the fact that there is a close similarity between acid-base reactions and oxidation-reduction reactions because both acids and oxidising agents have a tendency to accept a pair of electrons from bases and reducing agents respectively.

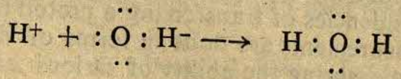
Examples

(*i*) The reaction between boron trifluoride, BF_3 and ammonia, NH_3



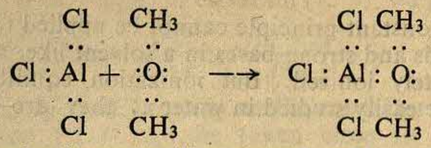
$$\underset{\text{acid}}{\begin{array}{c} F \\ \cdot\cdot \\ F:B \\ \cdot\cdot \\ F \end{array}} + \underset{\text{base}}{\begin{array}{c} H \\ \cdot\cdot \\ :N:N \\ \cdot\cdot \\ H \end{array}} \longrightarrow F:\begin{array}{c} F \\ \cdot\cdot \\ B \\ \cdot\cdot \\ F \end{array}:\begin{array}{c} H \\ \cdot\cdot \\ N \\ \cdot\cdot \\ H \end{array}:H$$

(*ii*) The reaction between H^+ and OH^- ions



$$H^+ + :\begin{array}{c} \cdot\cdot \\ O \\ \cdot\cdot \end{array}:H^- \longrightarrow H:\begin{array}{c} \cdot\cdot \\ O \\ \cdot\cdot \end{array}:H$$

(*iii*) The reaction between aluminium trichloride and dimethyl ether



$$\begin{array}{c}Cl\\ \cdot\cdot\\ Cl:Al\\ \cdot\cdot\\ Cl\end{array} + \begin{array}{c}CH_3\\ \cdot\cdot\\ :O:\\ \cdot\cdot\\ CH_3\end{array} \longrightarrow \begin{array}{cc}Cl & CH_3\\ \cdot\cdot & \cdot\cdot\\ Cl:Al: & O:\\ \cdot\cdot & \cdot\cdot\\ Cl & CH_3\end{array}$$

(*iv*) The reaction between silicon tetrafluoride and fluoride ion

$$\underset{\text{acid}}{SiF_4} + \underset{\text{base}}{2\,:\ddot{\underset{\cdot\cdot}{F}}:^-} \longrightarrow Si\,F_6^{2-}$$

Lewis theory is much broader in scope than Bronsted-Lowry theory because the Lowry theory focuses attention on the electron pair rather than on the proton.

15.3. HARD AND SOFT ACIDS AND BASES

The difficulty of Lewis concept is that it cannot measure precisely the strength by a single type of reaction. This has, therefore, led to other means of classifying reactions of Lewis acids with Lewis bases. One of the most useful is the concept of hard and soft acids and bases. A hard acid is one in which the acceptor atom of the acid is small, has a high positive charge and has no valence electrons that can easily be shifted from their positions near the nucleus. Examples are Li^+, H_3O^+ and Al^{3+}.

Soft acids have large acceptor atoms, zero or small positive charge and several valence electrons, that can easily be shifted or removed. Examples are Ag^+, Hg^{2+} etc.

Hard bases are those that hold tightly to their valence electrons such as OH^- and F^-. Soft bases have positions of their valence electrons easily shifted by positive charges in their neighbourhood or even removed to other nuclei. Examples are I^- and CO. The guiding principle in these reactions is that a stable compound tend to be formed when hard acids combine with hard bases and soft acids combine with soft bases. Table 15.1 gives some common examples of hard and soft acids and bases.

TABLE 15.1

Acids and bases classified as hard and soft

Acids		*Bases*	
Hard	Soft	Hard	Soft
Li^+	Ag^+	OH^-	CH_3S^-
Mg^{2+}	Hg^{2+}	F^-	I^-
Al^{3+}	Tl^{3+}	NH_3	$(CH_3)_3P$
$AlCl_3$	$GaCl_3$	$(CH_3)_2O$	CO
BF_3	$InCl_3$	CH_3OH	CH_3SH
H_3O^+			

15.4. IONIZATION CONSTANTS OF ACIDS AND BASES

The equilibrium constant principle cannot be applied to the ionization of strong acids and strong bases in a solvent like water because they are completely ionized. But ionization equilibria of weak electrolytes can be easily studied in water as they are feebly dissociated.

(*i*) **Acids.** The ionization equilibria of any weak monobasic acid HA such as acetic acid dissolved in water can be represented by the equation

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

The equilibrium constant in terms of activities is given by

$$K = \frac{a_{H_3O^+} \times a_{A^-}}{a_{HA} \times a_{H_2O}} \qquad \ldots (15.5)$$

If the solution is dilute, water will be in excess and hence the activity of water a_{H_2O} may be taken equal to its concentration, which is a constant (k). Thus

$$K = \frac{a_{H_3O^+} \times a_{A^-}}{a_{HA} \times k} \qquad \ldots (15.6)$$

Replacing the product of the constants K and k by K_a, we get the simple expression

$$K_a = \frac{a_{H_3O^+} \times a_{A^-}}{a_{HA}}$$

The constant K_a is known as the ionization constant of the acid, *HA*. For further simplicity, $a_{H_3O^+}$ can be replaced by a_{H^+} subject to the condition that a_{H^+} *refers to the activity of hydrogen ion in solution and not to a proton.*

Therefore, more simplified form of the ionization constant K_a of the acid is written as

$$K_a = \frac{a_{H^+} \times a_{A^-}}{a_{HA}} \qquad \ldots (15.7)$$

Replacing the activities by the product of corresponding concentrations (C) and activity coefficients (f), equation (15.7) becomes

$$K_a = \frac{(C_{H^+} \times f_{H^+})(C_{A^-} \times f_{A^-})}{(C_{HA} \times f_{HA})}$$

$$= \frac{C_{H^+} \times C_{A^-}}{C_{HA}} \times \frac{f_{H^+} \times f_{A^-}}{f_{HA}} \qquad \ldots (15.8)$$

If C is the original concentration of the acid HA in water and α is its degree of dissociation, then at equilibrium

$$C_{HA}=C(1-\alpha) \text{ and } C_{H^+}=C_{A^-}=C\alpha$$

Substituting these values in equation (15.8), we get

$$K_a=\frac{\alpha^2 C}{1-\alpha}\times\frac{f_{H^+}\times f_{A^-}}{f_{HA}} \qquad \ldots (15.9)$$

For dilute solution, the activity coefficient factor on the right hand side of equation (15.9) can be taken close to unity. Therefore, equation (15.9) can be rewritten as

$$K_a=\frac{\alpha^2 C}{1-\alpha} \qquad \ldots (15.10)$$

Again for weak acids, α will be very small and $1-\alpha\approx 1$. Under these conditions, the equation for α reduces to

$$K_a=\alpha^2 C \qquad \ldots (15.11)$$

Knowing α and C, it is possible to calculate K_a from equation (15.11).

Equation (15.11) can also be utilized for comparing the strengths of two weak acids in the common aqueous solution having same concentration. If α_1 is the degree of dissociation of one acid having concentration C and α_2 is the degree of dissociation of another acid of equal concentration, then from equation (15.11), the ratio of the two degrees of dissociation is given by

$$\frac{\alpha_1}{\alpha_2}=\sqrt{\frac{K_{a_1}}{K_{a_2}}} \qquad \ldots (15.12)$$

where K_{a_1} and K_{a_2} are the ionization constants of the two acids taken into consideration.

But α is a measure of strength of an acid. Therefore,

$$\frac{\text{Strength of acid}_1}{\text{Strength of acid}_2}=\sqrt{\frac{K\text{acid}_1}{K\text{acid}_2}}$$

(*ii*) **Polybasic acids**. Polybasic acids are those which contain two or more ionisable hydrogen atoms. They do not ionize in a single step, but in successive stages depending on the number of protons. Consider, for example, the dissociation of carbonic acid. It being a dibasic acid, ionizes in two steps as shown below:

1st Stage $\quad H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$

2nd Stage $\quad HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$

The corresponding ionization constants of the two stages are given by

$$K_{a_1}=\frac{a_{H^+}\times a_{HCO_3^-}}{a_{H_2CO_3^-}}$$

and

$$K_{a_2}=\frac{a_{H^+}\times a_{CO_3^{2-}}}{a_{HCO_3^-}}$$

Similarly the dissociation of tribasic acid, for example, phosphoric acid, takes place in three stages as given below:

1st Stage $H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$

2nd Stage $H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$

3rd Stage $HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$

The corresponding ionization constants are given by

$$K_{a_1} = \frac{a_{H^+} \times a_{H_2PO_4^-}}{a_{H_3PO_4}}$$

$$K_{a_2} = \frac{a_{H^+} \times a_{HPO_4^{2-}}}{a_{H_2PO}}$$

and $$K_{a_3} = \frac{a_{H^+} \times a_{PO_4^{3-}}}{a_{HPO_4^{2-}}}$$

The values of the ionization constants can be determined by conductance measurements. It has been found that in any dibasic acid, the dissociation is more complete in the first stage than in the second stage ($K_{a_1} > K_{a_2}$) while in any tribasic acid, the dissociation in first stage is greater than in second stage and that in the second stage is greater than in third stage ($K_{a_1} > K_{a_2} > K_{a_3}$). Each stage involves a true equilibrium between the ionized particles and the unionized molecules. In the case of sulphuric acid which being a strong acid, dissociation is complete in the first stage but dissociation in the second stage is incomplete and hence K_{a_2} can be calculated.

But in phosphoric acid (weak acid), each stage involves a partial ionization and hence the three ionization constants can be determined. The values of these ionization constants at 25°C are $K_{a_1} = 7.52 \times 10^{-3}$, $K_{a_2} = 6.22 \times 10^{-8}$ and $K_{a_3} = 4.8 \times 10^{-13}$.

The reason for the decrease in values of ionization constants in successive stages lies in the fact that tendency for the loss of proton is maximum for uncharged molecules, *e.g.*, H_3PO_4, and decreases as the negative charge on the molecules, from which the detachment of the proton is to take place, increases. As the negative charge on the molecules increases, electrostatic attraction will also increase and thus the removal of electron will also become more and more difficult in the successive stages.

Ionization constants of some weak acids at 25°C are given in Table 15.2.

(*iii*) **Bases.** Consider a weak base BOH, such as ammonium hydroxide. Its ionization can be represented by the equation

$$BOH \rightleftharpoons B^+ + OH^-$$

The ionization constant, K_b of the base is given by

$$K_b = \frac{a_{B^+} \cdot a_{OH^-}}{a_{BOH}}$$

As in weak acids, the equation for K_b can also be written as

$$K_b = \frac{\alpha^2 C}{(1-\alpha)} \times \frac{f_{B^+} \cdot f_{OH^-}}{f_{BOH}}$$

Again for dilute solutions, activity coefficient of each component will be approximately equal to unity. Therefore,

$$K_b = \frac{\alpha^2 C}{(1-\alpha)}$$

TABLE 15.2

Ionization constants of some weak acids at 25°C

Acid	*Formula*	K_{a_1}	K_{a_2}	K_{a_3}
Acetic acid	CH_3COOH	1.75×10^{-5}		
Formic acid	$HCOOH$	1.774×10^{-4}		
Boric acid	H_3BO_3	5.80×10^{-10}		
Benzoic acid	C_6H_5COOH	6.29×10^{-5}		
Chloro acetic acid	$CH_2Cl.COOH$	1.38×13^{-3}		
Dichloro acetic acid	$CHCl_2.COOH$	5×10^{-2}		
Hydrocyanic acid	HCN	7.2×10^{-10}		
Carbonic acid	H_2CO_3	4.52×10^{-7}	4.69×10^{-11}	
Oxalic acid	$H_2C_2O_4$	5.02×10^{-2}	5.18×10^{-5}	
Phthalic acid	$C_6H_4(COOH)_2$	1.29×10^{-3}	3.80×10^{-8}	
Phosphoric acid	H_3PO_4	7.52×10^{-3}	6.22×10^{-6}	4.8×10^{-13}
Sulphuric acid	H_2SO_4	Strong	1.01×10^{-2}	

TABLE 15.3

Ionization constants of some weak bases at 25°C

Base	*Formula*	K_b
Ammonia	NH_4OH	1.81×10^{-5}
Methyl Amine	CH_3NH_2	4.38×10^{-4}
Dimethyl Amine	$(CH_3)_2NH$	5.12×10^{-4}
Trimethyl Amine	$(CH_3)_3N$	5.21×10^{-5}
Aniline	$C_6H_5.NH_2$	3.83×10^{-10}
Pyridine	C_6H_5N	1.4×10^{-9}
Urea	NH_2CONH_2	1.5×10^{-4}

Hence from the knowledge of α and C, K_b can be calculated.

Ionization constants of some weak base at 25°C are given in Table 15.3.

15.5. IONIZATION OF WATER (IONIC PRODUCT OF WATER)

We know that water is a substance which can act both as an acid and a base, so it is not surprising that in all aqueous solutions as in water, the equilibrium shown below exists.

$$H_2O+H_2O \rightleftharpoons H_3O^++OH^- \qquad \ldots (15.13)$$

For simplicity and convenience, the ionization of water is generally represented by the equation

$$H_2O \rightleftharpoons H^++OH^- \qquad \ldots (15.14)$$

Conductance measurements and other evidence show that the reaction proceeds to a small but easily measurable extent.

Applying the Law of Mass Action, the equilibrium constant is given by

$$K=\frac{a_{H^+}a_{OH^-}}{a_{H_2O}} \qquad \ldots (15.15)$$

However, since water is dissociated to a very small extent, its activity in an aqueous solution may be regarded as constant. Including this constant in K, equation (15.15) becomes

$$K_W=a_{H^+}\times a_{OH^-} \qquad \ldots (15.16)$$

The constant K_W is known as the ionic product of water. It indicates that in pure water or in any aqueous solution, both hydrogen and hydroxyl ions are present and the product of their activities is always constant at given temperature. For dilute solutions, the activities can be replaced by the corresponding concentrations. In terms of concentrations, the constant is written as

$$K'_W=C_{H^+}\times C_{OH^-} \qquad \ldots (15.17)$$

The value of the ionic product of water can be easily measured by various methods based on conductance measurements and E.M.F. measurements. A list of the values of K_W at various temperatures is given in Table 15.4.

From the table, we find that the value of K_W increases rapidly with increasing temperature. At 25°C which is generally the experimental temperature, $K_W=1\times10^{-14}$. Again, pure water is neither acidic nor basic and hence will have equal concentrations of hydrogen ions and hydroxyl ions at any temperature. Therefore, at 25°C, $C_{H^+}\times C_{OH^-}=1\times10^{-14}$ gram ion per litre.

An aqueous solution in which $C_{H^+}=C_{OH^-}=1\times10^{-7}$ is said to be

TABLE 15.4.

Temperature °C	K_w
0°C	0.114×10^{-14}
10°C	0.292×10^{-14}
20°C	0.681×10^{-14}
25°C	1.008×10^{-14}
30°C	1.468×10^{-14}
40°C	2.919×10^{-14}
50°C	5.474×10^{-14}

neutral. When $C_{H^+} > C_{OH^-}$, the solution is acidic and when $C_{H^+} < C_{OH^-}$, the solution is basic. But irrespective of the fact that whether the solution is acidic or basic, the ionic product of water is always constant at a constant temperature.

The ionic product principle is of great importance and can be applied to any solution containing water for the calculation of concentrations of hydrogen ions and hydroxyl ions.

15.6. THE pH SCALE

Since hydrogen ion concentration of a solution can vary within very wide limits (from 1 gram ion to 10^{-14} gram ion per litre in solutions), it becomes essential to devise a scale which can express hydrogen ion concentration in a convenient way. Sorensen in 1909 suggested the use of the pH scale with the help of which one can very conveniently express hydrogen ion concentrations. In its original form, *the pH of a solution is defined as the negative logarithm to the base 10 of the hydrogen ion concentration in gram ions per litre.*

Thus

$$\text{pH} = -\log_{10} C_{H^+} \qquad \ldots (15.18)$$

Now a days, the concentration term is replaced by the activity and the modified form of the pH scale is

$$\text{pH} = -\log_{10} a_{H^+} \qquad \ldots (15.19)$$

It can also be written as

$$a_{H^+} = 10^{-\text{pH}}$$

Thus, if the pH of a solution is 4, $a_{H^+} = 10^{-4}$ while if the pH of a solution is 11, $a_{H^+} = 10^{-11}$.

In the same manner, the activity of hydroxyl ions, ionization constants of acids and bases, and the ionic product of water can be given logarithmic expressions; thus

$$\text{pOH} = -\log_{10} a_{\text{OH}^-}, \qquad \text{pK}_a = -\log_{10} \text{K}_a$$

and

$$\text{pK}_W = -\log_{10} \text{K}_W \qquad \ldots (15.20)$$

Since in any aqueous solution, the ionic product of water is expressed as

$$a_{H^+} . a_{OH^-} = K_W$$

or $-\log_{10} a_{H^+} - \log_{10} a_{OH^-} = -\log_{10} K_W$ . . . (15.21)

Using equations (15.19) and (15.20), we get

$$pH + pOH = pK_W \quad \text{. . . (15.22)}$$

It follows from equation (15.22) that the sum of pH and pOH for any aqueous solution is always constant and is equal to pK_W.

At a temperature of 25°C,

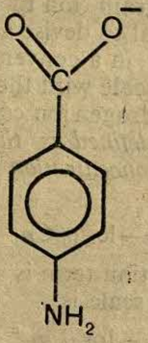
$$K_w = 10^{-14}$$

Hence $pH + pOH = 14$

For a neutral aqueous solution, $pH = pOH = 7$ while if the solution is acidic, $pH < 7$ and if the solution is basic, $pH > 7$.

pH and Drug Action

A number of drugs are either weak acids or weak bases, such as phenols, sulphonamides, alkaloids, *e.g.* codeine and barbiturates *e.g.* phenobarbitone. The extent to which such drugs are ionised depends upon their pK_a values and the pH of the medium in which they are used.



P—aminobenzoate

When the effect of pH on the toxic power of a drug is investigated, the results often suggest that the effective agent is either (*i*) the non-ionised form, or (*ii*) the ionised form or (*iii*) both forms of the drug. A number of drugs e.g , phenols are active against certain organisms in both the ionised and nonionised forms, although the neutral molecule is often much more active than the ion. The antifungal activity of 2, 4 dinitrophenol is a case in point. The biological active form of p-aminobenzoic acid, pK_a 4.8, is probably the anion. Neutral molecules usually penetrate cell membranes much more readily than do ions, because ions being hydrated have a greater size and depending on their charge, are either repelled by or adsorbed by the charged protein in the membrane.

Problem 15.1. Find the pH of the following solutions:

(*i*) 0.1 N HCl; (*ii*) 0.0032 M H_2SO_4; and (*iii*) 0.05 N HNO_3.

Solution. (*i*) $pH = -\log_{10} C_{H^+}$

In 0.1 N HCl; $C_{H^+} = 0.1$

$\therefore \quad pH = -\log 0.1 = 1$

(*ii*) Since molecular weight of H_2SO_4 is twice its equivalent weight, therefore 0.0032 M H_2SO_4 is same as 0.0064 N H_2SO_4.

In 0.0064 N H_2SO_4, $C_{H^+} = 0.0064$ or 6.4×10^{-3}

$\therefore pH = -\log_{10} 6.4 \times 10^{-3} = 3 - 0.8062 = 2.1938$

(*iii*) In 0.05 N HNO_3, $C_{H^+} = 0.05$

$\therefore pH = -\log_{10} 0.05 = 1.3010$

15.7. COMMON ION EFFETS

If to a solution of a weak acid or a weak base, some ions common to the acid or base are added, the degree of dissociation of acid or base is suppressed. Thus, if to a solution of acetic acid, some acetate ions are added in the form of sodium acetate, the dissociation of acetic acid is very much reduced. Similarly, hydrogen ions added in the form of hydrochloric acid will also suppress the dissociation of the acid. This effect on the dissociation of the acid or base on the addition of the common ion is referred to as the *common ion effect* and is an example of Le-Chatelier's principle.

Similarly, when solutions of two electrolytes with a common ion are mixed, the degree of dissociation of each of them is suppressed but the effect is more marked for the weaker of the two electrolytes.

The equilibrium

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

will shift to the left by an increase in the concentration of acetate ions or hydrogen ions.

Similarly, the equilibrium

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

will also shift to the left by an increase in the concentration of ammonium ions or hydroxyl ions.

Problem 15.2. The dissociation constant of acetic acid at 25°C is 1.75×10^{-5}. Calculate the degree of dissociation and the pH of the solution in a 0.500 M acetic acid solution.

Solution. For the reaction

$$CH_3COOH+H_2O \rightleftharpoons CH_3COO^-+H_3O^+$$

the equilibrium condition is

$$K_a=\frac{[CH_3COO^-]\,[H_3O^+]}{[CH_3COOH]}$$

If c is the initial conc. of acetic acid and α is its degree of dissociation then $[CH_3COO^-]=[H_3O^+]=c\alpha$

$$[CH_3COOH]=c(1-\alpha).$$

$$\therefore \quad K_a=\frac{c\alpha\, c\alpha}{c(1-\alpha)}\simeq c\alpha^2 \text{ or } \alpha=\sqrt{\frac{K_a}{c}}$$

Here $K_a=1.75\times10^{-5}$ and $c=0.500$

so that

$$\alpha=\sqrt{\frac{1\ 75\times10^{-5}}{.5}}=5.92\times10^{-3}$$

$$pH=-\log[H_3O^+]=-\log(c\alpha)$$

$$=-\log(0.500\times5.92\times10^{-3})=2.529.$$

Problem 15.3. A solution is 0.1 molar in HCN and 0.1 molar in NaCN. Calculate the concentration of hydrogen and hydroxyl ion if the ionization constant of HCN is 7.2×10^{-10}.

Solution. NaCN, being a strong electrolyte, completely dissociates to give 0.1 mole of CN^-. Cyanide ions are also produced by the ionization of HCN. If α is the degree of ionization, then

$$[CN^-]=0.1+\alpha C$$

$$[H^+]=\alpha C$$

and

$$[HCN]=C(1-\alpha)$$

$$\therefore \quad K_a=\frac{\alpha C.(0.1+\alpha C)}{C(1-\alpha)}$$

Substituting the values of K_a and C, we have

$$7.2\times10^{-10}=\frac{\alpha(0.1+0.1\alpha)}{1-\alpha}$$

or

$$\alpha=7.2\times10^{-9}$$

and $[H^+]=C\alpha=7.2\times10^{-9}\times0.1=7.2\times10^{-10}$ moles/litre

and

$$[OH^-]=\frac{1\times10^{-14}}{7.2\times10^{-10}}=1.4\times10^{-5}\text{ moles/litre}$$

15.8. BUFFER SOLUTIONS

It has been observed that even the purest form of water does not retain a constant value of pH=7 for a long time. This is due to the fact that the carbon dioxide from air or silicates from the glass containing water may dissolve in water thereby making the solution slightly acidic or basic respectively and pH will correspondingly be changed.

Since there are various chemical reactions and bio-chemical reactions in particular which can take place more rapidly in solutions of specific pH values, therefore, it becomes essential to have solutions which can maintain constant pH values even if some little acid or base is added. *Such solutions which are resistant to change of pH when some acid or base is added to them are called Buffer solutions or simply buffers.*

Buffer solutions are usually those solutions which contain a mixture of a weak acid and its salt such as acetic acid and sodium acetate or a weak base and its salt such as ammonium hydroxide and ammonium chloride. Solutions containing salt of a weak acid and a weak base, such as ammonium acetate, also have some buffer action.

In a qualitative manner, the buffer action of such solutions can be readily explained as follows:

(*i*) *Buffer action of solutions containing a mixture of weak acid and its highly ionizable salt such as acetic acid and sodium acetate.* Such a solution will contain excess of acetate ions, a large amount of unionized acetic acid and a small amount of hydrogen ions (H_3O^+) formed by original ionization of acetic acid. When hydrogen ions are added to this solution in the form of some acid such as HCl, they will combine with the acetate ions to form more unionized acetic acid.

$$H_3O^+ + CH_3COO^- = H_2O + CH_3COOH$$

Thus hydrogen ions added are removed by excess of acetate ions already present and the solution will retain its constant pH value.

When some base, such as sodium hydroxide is added, the hydroxyl ions added will be removed by reaction with acetic acid.

$$OH^- + CH_3\,COOH = CH_3\,COO^- + H_2O$$

Thus, again the solution will maintain a constant pH value.

(*ii*) *Buffer action of solutions containing a mixture of weak base and its highly ionizable salt such as ammonium hydroxide and ammonium chloride.*

This solution will contain excess of ammonium ions, a large amount of unionized ammonium hydroxide and a small amount of hydroxyl ions.

On adding some strong acid such as HCl, the hydrogen ions added will be removed by ammonium hydroxide.

$$H_3O^+ + NH_4OH = NH_4^+ + 2H_2O$$

Thus the solution will suffer no change in pH.

Similarly, when a base is added, the hydroxyl ions added are removed by reacting with ammonium ions to form unionized ammonium hydroxide. Thus, the reaction

$$OH^- + NH_4^+ = NH_4OH$$

helps the solution to retain constant pH value.

(*iii*) *Buffer action of solutions containing salt of a weak acid and a weak base such as ammonium acetate.*

Such a solution will contain excess of both ammonium ions and acetate ions. If some acid is added, the hydrogen ions added will be removed by reaction with acetate ions and if some base is added, the added hydroxyl ions will be removed by ammonium ions as shown below:

$$H_3O^+ + CH_3COO^- = CH_3COOH + H_2O \text{ ; and}$$
$$OH^- + NH_4^+ = NH_4OH.$$

Thus in both the cases, the solution will not change its pH.

It should be remembered that the above considerationsare applicable only when the amount of acid or base added to the buffer solution is small.

Calculation of pH values of buffer solution. Consider a buffer solution containing a mixture of acetic acid and sodium acetate. Let C_1 and C_2 be the initial concentrations of the acid and salt, respectively. The pH value for this solution can be easily calculated from a knowledge of the ionization constant of the weak acid as follows:

The equilibrium expression for the dissociation of acetic acid for the buffer solution is

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \qquad \ldots (15.23)$$

or

$$[H^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]} \qquad \ldots (15.24)$$

where K_a is the ionization constant of the acid and the terms in the bracket stand for the concentrations of various species involved.

Now, since acetic acid is a weak acid, it will undergo dissociation to a very small extent. In the presence of sodium acetate which is completely dissociated, it can be assumed that acetic acid is not dissociated at all. Hence concentration of the unionized acetic acid can be taken equal to the initial concentration of the acid.

Thus, $[CH_3COOH] = C_1$ (initial concentration of the acid)

For the same reason, the concentration of the acetate ions can be taken approximately equal to the concentration of the salt. Thus,

$$[CH_3COO^-]_{CH_3COONa} \approx [CH_3COO^-]_{acid} + [CH_3COO^-]_{CH_3COONa}$$
$$= C_2 \text{ (initial concentration of the salt)}$$

Thus, hydrogen ion concentration from equation (15.24) with fair approximation is given by

$$[H^+] = K_a \frac{[\text{Acid}]}{[\text{Salt}]} \qquad \ldots (15.25)$$

where the terms in the brackets refer to the concentrations of the acid and the salt respectively. On taking the logarithms and reversing the signs throughout of equation (15.25), we get

$$-\log [H^+] = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

or $$\mathrm{pH}=pK_a+\log\frac{[\text{Salt}]}{[\text{Acid}]} \qquad \ldots (15.26)$$

Equation (15.26) is known as the Henderson-Hasselbalch equation. With the help of this equation, one can easily calculate the pH of the buffer solution by knowing ionization constant of the acid and the concentrations of the salt and acid. Alternately it can be employed to prepare solutions of desired pH values. As a rough rule, to prepare a buffer solution of given pH, we pick up an acid with $\mathrm{p}K_a \approxeq \mathrm{pH}$. We then calculate the ratio of concentration of the salt and the acid to be used.

Use of Buffer Solutions

Buffer solutions find numerous applications in the fields of analytical, pharmaceutical and biological systems. Buffer solutions are used for preparing standard solutions of definite pH values which are insentive towards the addition of small quantities of acids and alkalies. Many chemical reactions with organic reagents can be achieved only at a definite pH value of the solution. Citric acid is used for stabilishing milk of magnesia. Penicillin preparations are stabilised by the addition of sodium citrate or aluminium hydroxide. Sulphonamide preparations usually contain sodium bicarbonate, sodium acetate or sodium citrate which act as buffers. Buffer solutions are immensely employed in the formulation of Opthalmic preparations.

Blood is maintained at a pH of about 7.4 by the buffers in the plasma. The plasma contains carbonic acid, carbonate and sodium salts of phosphoric acid as buffers. Tears have been found to have a great degree of buffer capacity, allowing a dilution of 1 : 15 with neutral distilled water before an alteration of pH is noticed.

Problem 15.4. A buffer solution was obtained by 8.3 gms of acetic acid and 16.0 gms of scdium acetate. The buffer is diluted to one litre. Calculate the pH of the solution if 0.70 ml of IM HCl is added to it. The dissociation constant of acetic acid is 1.8×10^{-5}. (Molecular weights of acetic acid and sodium acetate are respectively 60 and 82).

Solution. $$\mathrm{pH}=pK_a+\log_{10}\frac{[\text{Salt}]}{[\text{Acid}]}$$

Here, $$pK_a=-\log_{10}K_a=-\log_{10}(1.8\times10^{-5})=4.7447$$

$$[\text{Salt}]=\frac{16.0}{82}=0.1950 \text{ gm mole}$$

$$[\text{Acid}]=\frac{8.3}{60}=0.1383 \text{ gm mole}$$

On adding 0.7 ml of 1N HCl. we have moles of HCl added=0.7 ml of 1 molar =0.0007 gm mole. (Increase in volume on adding HCl is negligible.)

Thus, on adding HCl, concentration of the H^+ increases by 0.0007 gm ion. The concentrations of salt and acid, then, become

$$[\text{Acid}]=0.1383+0.0007=0.1390$$
$$[\text{Salt}]=0.1950-0.0007=0.1943$$
$$\therefore \quad \mathrm{pH}=pK_a+\log_{10}\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$=4.7447+\log_{10}\frac{0.1943}{0.1390}$$

$$=4.7447+0.1455=4.8902$$

15.9. HYDROLYSIS

When an acid reacts with a base in an aqueous solution, neutralization takes place. This neutralization is complete only in the case of reaction between strong acid like hydrochloric acid and strong base like sodium hydroxide and the final solution will be neutral *i.e.*, one containing equal number of hydrogen ions and hydroxyl ions. In all other cases, the final solution will not be neutral and is either acidic or basic. Thus, when a weak acid like acetic acid is neutralized by a strong base like sodium hydroxide, the final solution is found to be alkaline and when a weak base like ammonium hydroxide is neutralized by a strong acid like hydrochloric acid, the final solution is found to be acidic. Similarly, if both the acid and base are weak, the neutralization will not be complete and the final solution will be either acidic or alkaline depending on the relative strengths of the acid and base. The acidity or basicity of a final solution is due to the tendency of the salt formed by neutralization to react with water thereby partially reversing the process of neutralization. *This partial reversal of neutralization due to the reaction of the salt with water is known as the hydrolysis.* When the solvent is not water, the phenomenon is generally referred to as *solvolysis*.

For a study of hydrolytic behaviour of various salts, four types of combination are considered.

(*i*) Salts of strong acids and strong bases such as sodium chloride.

(*ii*) Salts of weak acids and strong bases such as sodium acetate.

(*iii*) Salts of strong acids and weak bases such as ammonium chloride; and

(*iv*) Salts of weak acids and weak bases such as ammonium acetate.

(*i*) **Salts of strong acids and strong bases.** Consider, for example, the hydrolytic behaviour of sodium chloride—a salt formed by combination of strong acid HCl and strong base NaOH. In aqueous solution, it is ionized into sodium ions and chloride ions. These ions do not react with H^+ and OH^- from water because the possible products of such interactions, namely, sodium hydroxide and hydrochloric acid, being strong electrolytes, would be completely ionized. The products would again be sodium and chloride ions and hydrogen and hydroxyl ions would recombine to form water. Thus the products of hydrolysis would be identical with the reactants and consequently there will be no change in the concentrations of hydrogen and hydroxyl ions. Therefore, *salts of strong acids and strong bases do not undergo hydrolysis and the solutions of such types of salts are neutral.*

(*ii*) **Salts of weak acids and strong bases**. Salts of weak acids and strong bases such as sodium acetate, sodium carbonate, sodium cyanide etc., undergo hydrolysis to give basic solution. Consider, for example, the hydrolysis of sodium acetate. In solution, it is ionized to give Na^+ and CH_3COO^-. Sodium ions will not undergo hydrolysis because on reaction with OH^-, they form NaOH which being a strong electrolyte, is highly ionized to give again Na^+ and OH^-. However, the acetate ions will react with water to form feebly ionized acetic acid and lead to the formation of hydroxyl ions:

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

These OH^- make the solution alkaline.

Actually CH_3COO^- reacts with H_3O^+ from the water resulting in the excess of OH^- over H_3O^+. The undissociated water will further ionize to maintain constant value of the equilibria ($K_W = C_{H_3O^+} C_{OH^-}$). This is shown as below:

(*a*) $$H\ O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

(*b*) $$CH_3COO^- + H_3O^+ \rightleftharpoons \underset{\text{(feebly ionized)}}{CH_3COOH} + OH^-$$

Removal of H_3O^+ by CH_3COO^-, as shown in reaction (*b*), will cause the equilibrium in reaction (*a*) to shift more towards right to yield more H_3O^+ and OH^-. CH_3COO^- will further react with H_3O^+ according to reaction (*b*) and thus this series of reactions will lead to an accumulation of OH^-. The solution, therefore, becomes alkaline.

Hydrolytic constant. Hydrolysis of sodium acetate is represented by

$$CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$$

Na^+, being common on both sides, can be cancelled and the equation takes the form

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

In general, if BA is the salt formed by combination of a weak acid HA and strong base BOH, the hydrolysis is due to the anion of the acid and is represented as

$$A^- + H_2O \rightleftharpoons HA + OH^- \qquad \ldots (15.27)$$

Applying the law of Mass Action to it and assuming activity of water to be constant, the equilibrium constant, K_h, is given by

$$K_h = \frac{a_{HA} . a_{OH^-}}{a_{A^-}} \qquad \ldots (15.28)$$

The constant K_h, known as the hydrolytic constant of the ion A^-, determines the extent to which the ion A^- will undergo hydrolysis. It can easily be shown that the magnitude of K_h depends on the ionization constant of the acid, K_a and the ionic product of water as follows :

Multiplying the numerator and denominator of the right hand side of equation (15.28) by a_{H^+}, we get

$$K_h=\left(\frac{a_{HA}}{a_{H^+}a_{A^-}}\right)(a_{H^+}\times a_{OH^-}) \qquad \ldots (15.29)$$

But since $$\frac{a_{H^+}\times a_{A^-}}{a_{HA}}=K_a \qquad \ldots (15.30)$$

(the ionization constant of the acid for the equilibria $HA \rightleftharpoons H^+ + A^-$)

and $$a_{H^+}.a_{GH^-}=K_W \qquad \ldots (15.31)$$

Therefore, equation (15.29) becomes

$$K_h=\frac{K_W}{K_a} \qquad \ldots (15.32)$$

Thus the hydrolytic constant can be determined by the ratio of the ionic product for water to the dissociation of the weak acid.

Degree of hydrolysis. The extent to which the salt hydrolyses is known as the degree of hydrolysis and is defined as *fraction of the total salt that undergoes hydrolysis when the equilibrium has been established.*

If C moles per litre is the initial concentration of the salt and h is its degree of hydrolysis, then for the equilibrium we have

$$\underset{C(1-h)}{A^-} + H_2O \rightleftharpoons \underset{Ch}{HA} + \underset{Ch}{OH^-}$$

Therefore, $$K_h=\frac{ChCh}{C(1-h)}$$

Since the solution is very dilute, the activity of water is taken as constant.

$$K_h=\frac{Ch^2}{1-h} \qquad \ldots (15.33)$$

When h is small, $(1-h)$ in the denominator can be approximately taken equal to unity. Therefore, equation (15.33) becomes

$$K_h=Ch^2 \text{ or } h=\sqrt{\frac{K_h}{C}} \qquad \ldots (15.34)$$

Since $K_h=\frac{K_W}{K_a}$, equation (15.34) can also be written as

$$h=\sqrt{\frac{K_W}{K_a.C}} \qquad \ldots (15.35)$$

With the help of equation (15.35), one can easily calculate the degree of hydrolysis of the salt from a knowledge of ionization constant of the acid and concentration of the salt.

Problem 15.5. Calculate the degree of hydrolysis of 0.1 N solution of KCN. Dissociation constant of HCN at 25°C is 7.2×10^{-10}.

Solution. We have, $K_h=\frac{K_w}{K_a}$

Here $K_w = 1.0 \times 10^{-14}$ and $K_a = 7.2 \times 10^{-10}$

$\therefore$ $$K_h = \frac{1.0 \times 10^{-14}}{7.2 \times 10^{-10}} = 1.38 \times 10^{-5}$$

To calculate the degree of hydrolysis

$\because$ $$K_h = Ch^2 \quad \text{or} \quad h = \sqrt{\frac{K_h}{C}}$$

$\therefore$ $$h = \sqrt{\frac{1.38 \times 10^{-5}}{0.1}} = 1.18 \times 10^{-2}$$

Degree of hydrolysis=1.18%.

(*iii*) **Salts of strong acids and weak bases.** Salts of strong acids and weak bases such as NH_4Cl, $CuSO_4$, $FeCl_3$ etc., undergo hydrolysis to give acidic solution. Consider, for example, the hydrolysis of ammonium chloride. In aqueous solution, it is ionized to give NH_4^+ and Cl^-. Chloride ions will not undergo hydrolysis because of the reasons already explained. However, ammonium ions will be hydrolysed to form feebly ionized NH_4OH and there will be excess of H_3O^+ in the solution as shown below:

$$NH_4^+ + 2H_2O \rightleftharpoons \underset{\text{(unionized)}}{NH_4OH} + H_3O^+$$

The presence of H_3O^+ makes the solution acidic.

This reaction can be explained more clearly as follows :

NH_4^+ reacts with OH^- from the water resulting in an excess of H_3O^+ over OH^-. The undissociated water will further ionize to maintain the constant value of K_W. This is shown by the following two reactions:

(*a*) $$H_2O + H_2O \rightleftharpoons H_3O + OH^-$$

(*b*) $$NH_4^+ + OH^- \rightleftharpoons NH_4OH$$

Removal of OH^- by NH_4^+ as shown in reaction (*b*) will cause the equilibrium in reaction (*a*) to shift more towards right to yield more H_3O^+ and OH^-. NH_4^+ will further react with OH^- according to reaction (*b*) and thus this series of reactions will lead to an accumulation of H_3O^+. The solution, therefore, becomes acidic.

Hydrolytic constant. Hydrolysis of ammonium chloride is represented by

$$NH_4^+ + 2H_2O \rightleftharpoons NH_4OH + H_3O^+$$

In general, the hydrolysis of salts of strong acids and weak bases is due to the cation of the bases and is represented as

$$B^+ + 2H_2O \rightleftharpoons BOH + H_3O^+ \qquad \ldots (15.36)$$

Applying the law of mass action and assuming the activity of water to be constant, the hydrolytic constant is given by

$$K_h = \frac{a_{BOH^-} . a_{H_3O^+}}{a_{B^+}} \qquad \ldots (15.37)$$

Multiplying the numerator and denominator of the right hand side of equation (15.37) by a_{OH^-}, we get

$$K_h=\left(\frac{a_{BOH}}{a_{B^+}.a_{CH^-}}\right)(a_{H_3O^+}.a_{OH^-}) \qquad \ldots (18.38)$$

Since,
$$\frac{a_{B^+}.a_{OH^-}}{a_{BOH}}=K_b$$

K_b is the ionization constant of the base for the equilibrium $BOH \rightleftharpoons B^+ + OH^-$

and
$$a_{H_3O^+}.a_{OH^-}=K_W$$

Equation (15.38) becomes $K_h=\dfrac{K_W}{K_b}$ $\qquad \ldots (15.39)$

Thus the hydrolytic constant of salts of strong acids and weak bases can be determined by the ratio of the ionic product of water to the ionization constant of the weak base.

Degree of hydrolysis. As in salts of type (*ii*), an equation analogous to equation (15.35) can be obtained. The expression in this case is

$$h=\sqrt{\frac{K_W}{K_b.C}} \qquad \ldots (15.40)$$

Problem 15.6. Given that the dissociation constant of NH_4OH at 25°C is 1.8×10^{-5}, calculate the hydrolysis constant and degree of hydrolysis of NH_4Cl in a 0.001 M solution. What will be the H^+ ion concentration of the solution?

Solution. $K_h=\dfrac{K_w}{K_b}=\dfrac{1.0\times10^{-14}}{1.8\times10^{-5}}=5.55\times10^{-10}$

Again, $h=\sqrt{\dfrac{K_h}{C}}$

$$=\sqrt{\frac{5.55\times10^{-10}}{0.0001}}$$

$$=7.45\times10^{-4}$$

Hence per cent hydrolysis $=0.0745\%$

H^+ ion concentration $=x.C$

$$=7.45\times10^{-4}\times0.0001$$

$$=7.45\times10^{-7} \text{ gm ion litre}^{-1}.$$

(*iv*) **Salts of weak acids and weak bases.** The hydrolysis of salts of weak acids and weak bases such as ammonium acetate is represented by

$$\underset{}{CH_3COO^-} + NH_4^+ + H_2O \rightleftharpoons \underset{\text{(feebly ionized)}}{CH_3COOH} + \underset{\text{(feebly ionized)}}{NH_4OH}$$

Here, both the ions are hydrolysed to form feebly ionized acetic acid and ammonium hydroxide. Whether the solution of such type of salt in water is acidic or basic is determined by the relative strengths of the acid and base. If they are equally strong the solution will be neutral.

Hydrolytic constant. The general expression for the hydrolysis of salts of weak acids and weak bases is

$$B^+ + A^- + H_2O \rightleftharpoons BOH + HA \qquad \ldots (15.41)$$

For this equilibrium, the hydrolytic constant, K_h, is given by

$$K_h = \frac{a_{BOH}.a_{HA}}{a_{B^+}.a_{A^-}} \qquad \ldots (15.42)$$

If the numerator and denominator of the right hand side of equation (15.42) are multiplied by $a_{H^+}.a_{OH^-}$, equation (15.42) becomes

$$K_h = \left(\frac{a_{BOH}}{a_{B^+}.a_{OH^-}}\right)\left(\frac{a_{HA}}{a_{H^+}.a_{A^-}}\right)(a_{H^+}.a_{OH^-}) \qquad \ldots (15.43)$$

But since, $\dfrac{a_{BOH}}{a_{B^+}.a_{OH^-}} = \dfrac{1}{K_b}$,

$\dfrac{a_{HA}}{a_{H^+}.a_{A^-}} = \dfrac{1}{K_a}$ and $a_{H^+}.a_{OH^-} = K_W$, equation (15.43) becomes

$$K_h = \frac{K_W}{K_a K_b} \qquad \ldots (15.44)$$

Thus, for salts of weak acids and weak bases, the hydrolytic constant is determined by the ionic product of water and the ionization constants of both the weak acids and weak bases.

Degree of hydrolysis. If C moles per litre is the initial concentration of the salt and h is its degree of hydrolysis, then at equilibrium, the various concentration terms are given as shown below:

$$\underset{C(1-h)}{B^+} + \underset{C(1-h)}{A^-} + H_2O \rightleftharpoons \underset{Ch}{BOH} + \underset{Ch}{HA} \qquad \ldots (15.45)$$

Therefore, $$K_h = \frac{Ch \times Ch}{C(1-h) \times C(1-h)}$$

or $$K_h = \frac{h^2}{(1-h)^2} \qquad \ldots (15.46)$$

Taking $1-h \simeq 1$, equation (15.40) becomes $K_h = h^2$

or $$h = \sqrt{K_h} = \sqrt{\frac{K_W}{K_a.K_b}} \qquad \ldots (15.47)$$

From equation (15.47), it is evident that degree of hydrolysis of salts of weak acids and weak bases is independent of the concentration of the salt taken.

Problem 15.7. Calculate the degree of hydrolysis of ammonium acetate, the dissociation constant of ammonium hydroxide is 1.80×10^{-5} and that for acetic acid is 1.8×10^{-5}; ionic product of water being 1.0×10^{-14}

Solution. Since ammonium acetate is a salt of weak acid and weak base:

$$K_h = \frac{K_w}{K_a K_b}$$

$$=\frac{1.0\times10^{-14}}{1.8\times10^{-5}\times1.8\times10^{-5}}=\frac{1.0\times10^{-4}}{1.8\times1.8}$$

For such a salt, degree of hydrolysis is given by

$$\frac{h}{1-h}=\sqrt{K_h}=\sqrt{\frac{1.0\times10^{-4}}{1.8\times1.8}}=\frac{10^{-2}}{1.8}=\frac{1}{180}$$

or $$h=0.0055.$$

15.10. HYDROGEN ION (ACID BASE) INDICATORS

Indicators are used to detect the equivalene point in titration of solutions of unknown strengths with a standard solution *i.e.*, a solution whose strength is exactly known. In acidimetric titrations, a hydrogen ion (or an acid-base) indicator is used. This indicator is a substance, which in certain limits, changes colour as the pH of the solution changes during the titration of an acid with a base. This offers a simple method for determining the pH of a solution by noting the colour of a suitable indicator when placed in that solution. The pH range, *i.e.*, the range over which the indicator changes colour is different for different indicators, *e g.*, the pH range of the indicator phenolphthalien is 8.3—10.5. If the pH of the solution is 8.3 or less, phenolphthalein will be colourless in the solution. But as the pH value rises above 8.3, phenolphthalein will develop a pink colour in the solution. Similarly, the pH range of indicator methyl orange is 3.2—4.5. If the pH value of solution is 3.2 or less, methyl orange will have red-colour but as the pH value of the solution rises above 4.5, the colour changes from red to yellow.

Theory of Indicators

Ostwald's theory (1891). According to Ostwald Theory, an acid-base indicator is a weak acid or a weak base and is partially dissociated in water to give hydrogen or hydroxyl ions. The degree of ionization can thus be altered by changing the concentration of these ions. Ostwald also pointed out that undissociated form of the indicator has a different colour from the dissociated form.

Let H*In* represent the unionized form of an indicator which is a weak acid. Its ionization in water is represented by

$$\mathrm{H}In+\mathrm{H_2O}\rightleftharpoons\mathrm{H_3O^+}+\mathrm{I}n^-$$

The unionized molecule, H*In* differs in colour from its conjugate base, $\mathrm{I}n^-$.

The above equilibrium, like the equilibrium in any other weak acid, is governed by the Law of Mass Action. The equilibrium constant, K_{In}, for the above equilibrium is given by

$$K_{In}=\frac{[\mathrm{H_3O^+}][\mathrm{I}n^-]}{[\mathrm{HI}n]}\qquad\ldots(15.48)$$

where the constant K_{In} is known as Indicator Constant and the various terms in the brackets stand for the concentration of the respective species. In writing equation (15.48), activity has been assumed to be equal to concentration.

Upon rearrangement equation, (15.48) becomes

$$[H_3O^+]=K_{I_n}\ \frac{[HIn]}{[In^-]}$$

$$=\frac{[\text{Form with acid colour}]}{[\text{From with alkaline colour}]}\qquad \ldots (15.49)$$

It is evident from equation (15.49) that the colour of the indicator at any hydrogen ion concentration of the solution depends on the ratio of concentrations of H*In* and *In*⁻ present at equilibrium.

If the indicator solution contains an excess of hydrogen ions, the equilibrium will shift from right to left and the ionization of H*In* will be suppressed. The solution would then contain a large excess of unionized H*In* molecules and will exhibit the colour or the acid form. Upon adding OH^- ions to the acidic solution containing the indicator, the original acid will be eventually neutralized. At this stage [H*In*] will be equal to [In^-] and the solution will show the neutral colour of the indicator. Further addition of OH^- ions will make the solution alkaline. The excess OH^- ions will combine with H_3O^+ ions and reduce their concentrations. The equilibrium will now shift more to the right and the solution will have an excess of In^- ions. Thus the alkaline solution will have the colour of the ionized form of the indicator.

Consider, for example, the indicator phenolphthalein. It is supposed to be a weak acid, its dissociation is represented by

$$\underset{\text{Colourless}}{HPh}+H_2O\rightleftharpoons H_3O^+ + \underset{\text{Pink}}{Ph^-}$$

The undissociated form of phenolphthalein is colourless while the dissociated form is pink. When the solution contains an excess of hydrogen ions, the equilibrium will be more on the left side and the solution will contain an excess of HPh molecules. Thus the acidic solution containing phenolphthalein will be colourless. Addition of hydroxyl ions will cause the removal of H_3O^+ ions and the equilibrium will shift towards the right. When there are excess of OH^- ions, the solution will show pink colour due to an excess of Ph^- ions present.

Phenolphthalein can be used satisfactorily in the titrations of strong acids *versus* strong bases. But in the case of ammonia or any other weak base, it is not suitable. This is due to the fact that the weak base will not furnish sufficient OH^- ions to shift the equilibrium towards right side at the end point of the titration and hence such a situation will not develop pink colour exactly at the end of the titration. Moreover, near the end point of the titrations, hydrolysis of the salt formed between NH_4^+ or any other cation of the weak base and Ph^- takes place which will prevent the formation of Ph^- ions as shown below:

$$NH_4^+ + Ph^- + H_2O\rightleftharpoons HPh+NH_4OH$$

$$=\frac{1.0\times10^{-14}}{1.8\times10^{-5}\times1.8\times10^{-5}}=\frac{1.0\times10^{-4}}{1.8\times1.8}$$

For such a salt, degree of hydrolysis is given by

$$\frac{h}{1-h}=\sqrt{K_h}=\sqrt{\frac{1.0\times10^{-4}}{1.8\times1.8}}=\frac{10^{-2}}{1.8}=\frac{1}{180}$$

or $$h=0.0055.$$

15.10. HYDROGEN ION (ACID BASE) INDICATORS

Indicators are used to detect the equivalene point in titration of solutions of unknown strengths with a standard solution *i.e.*, a solution whose strength is exactly known. In acidimetric titrations, a hydrogen ion (or an acid-base) indicator is used. This indicator is a substance, which in certain limits, changes colour as the pH of the solution changes during the titration of an acid with a base. This offers a simple method for determining the pH of a solution by noting the colour of a suitable indicator when placed in that solution. The pH range, *i.e.*, the range over which the indicator changes colour is different for different indicators, *e g.*, the pH range of the indicator phenolphthalien is 8.3—10.5. If the pH of the solution is 8.3 or less, phenolphthalein will be colourless in the solution. But as the pH value rises above 8.3, phenolphthalein will develop a pink colour in the solution. Similarly, the pH range of indicator methyl orange is 3.2—4.5. If the pH value of solution is 3.2 or less, methyl orange will have red-colour but as the pH value of the solution rises above 4.5, the colour changes from red to yellow.

Theory of Indicators

Ostwald's theory (1891). According to Ostwald Theory, an acid-base indicator is a weak acid or a weak base and is partially dissociated in water to give hydrogen or hydroxyl ions. The degree of ionization can thus be altered by changing the concentration of these ions. Ostwald also pointed out that undissociated form of the indicator has a different colour from the dissociated form.

Let H*In* represent the unionized form of an indicator which is a weak acid. Its ionization in water is represented by

$$HIn+H_2O\rightleftharpoons H_3O^+ + In^-$$

The unionized molecule, H*In* differs in colour from its conjugate base, In^-.

The above equilibrium, like the equilibrium in any other weak acid, is governed by the Law of Mass Action. The equilibrium constant, K_{In}, for the above equilibrium is given by

$$K_{In}=\frac{[H_3O^+][In^-]}{[HIn]} \qquad \ldots (15.48)$$

where the constant K_{In} is known as Indicator Constant and the various terms in the brackets stand for the concentration of the respective species. In writing equation (15.48), activity has been assumed to be equal to concentration.

Upon rearrangement equation, (15.48) becomes

$$[H_3O^+]=K_{I_n}\ \frac{[HIn]}{[In^-]}$$

$$=\frac{\text{[Form with acid colour]}}{\text{[From with alkaline colour]}} \quad \ldots (15.49)$$

It is evident from equation (15.49) that the colour of the indicator at any hydrogen ion concentration of the solution depends on the ratio of concentrations of H*In* and *In*⁻ present at equilibrium.

If the indicator solution contains an excess of hydrogen ions, the equilibrium will shift from right to left and the ionization of H*In* will be suppressed. The solution would then contain a large excess of unionized H*In* molecules and will exhibit the colour or the acid form. Upon adding OH^- ions to the acidic solution containing the indicator, the original acid will be eventually neutralized. At this stage [H*In*] will be equal to [*In*⁻] and the solution will show the neutral colour of the indicator. Further addition of OH^- ions will make the solution alkaline. The excess OH^- ions will combine with H_3O^+ ions and reduce their concentrations. The equilibrium will now shift more to the right and the solution will have an excess of In^- ions. Thus the alkaline solution will have the colour of the ionized form of the indicator.

Consider, for example, the indicator phenolphthalein. It is supposed to be a weak acid, its dissociation is represented by

$$\underset{\text{Colourless}}{HPh}+H_2O\rightleftharpoons H_3O^+ + \underset{\text{Pink}}{Ph^-}$$

The undissociated form of phenolphthalein is colourless while the dissociated form is pink. When the solution contains an excess of hydrogen ions, the equilibrium will be more on the left side and the solution will contain an excess of HPh molecules. Thus the acidic solution containing phenolphthalein will be colourless. Addition of hydroxyl ions will cause the removal of H_3O^+ ions and the equilibrium will shift towards the right. When there are excess of OH^- ions, the solution will show pink colour due to an excess of Ph^- ions present.

Phenolphthalein can be used satisfactorily in the titrations of strong acids *versus* strong bases. But in the case of ammonia or any other weak base, it is not suitable. This is due to the fact that the weak base will not furnish sufficient OH^- ions to shift the equilibrium towards right side at the end point of the titration and hence such a situation will not develop pink colour exactly at the end of the titration. Moreover, near the end point of the titrations, hydrolysis of the salt formed between NH_4^+ or any other cation of the weak base and Ph^- takes place which will prevent the formation of Ph^- ions as shown below:

$$NH_4^+ + Ph^- + H_2O \rightleftharpoons HPh + NH_4OH$$

Thus the pink colour is developed only when an excess of NH_4OH or any other weak base has been added.

Similarly, methyl orange which is supposed to be a weak base is not suitable in the titration of a weak acid against a strong base. Its ionization is represented by the equilibrium.

$$\underset{\text{Yellow}}{MeOH} \rightleftharpoons \underset{\text{Red}}{Me^+} + OH^-$$

If the solution is acidic, the equilibrium will be more on the right side and the solution will show red colour due to an excess of Me^+ ion. On the other hand, if the solution is alkaline, the equilibrium will shift towards the left side and the solution will be yellow in colour due to an excess of undissociated form of the indicator.

Useful ranges of the indicator. Taking negative logarithms throughout, equation (15.49) gives:

$$pH = pK_{I_n} + \log \frac{[In^-]}{[HIn]} \qquad \ldots (15.50)$$

The factor $pKI_n = -\log KI_n$ is known as indicator exponent. It is apparant from equation (15.50) that the ratio $[In^-]/HIn]$, which determines the colour of the solution, can be determined by the pH of the solution. The two forms of the indicator can be easily detected through naked eyes only under extreme cases, *i.e.*, either $[HIn] \gg [In^-]$ or $[In^-] \gg [HIn]$. In between these two extreme cases, the solution will show varying shades of colour intermediate between the acid form and the basic form which cannot be easily realised through naked eyes. In other words, the indicator does not change its colour sharply at a definite pH but changes gradually over a range of pH. As a rough rule, it is assumed that gradations of colour are detectable when the ratio $[HIn/In^-]$ is between 0.1 and 10. When the ratio is 0.1 or less, the solution will be alkaline and has the colour of In^-. Likewise, if the ratio is 10 or greater, the solution is acidic and has the colour of HIn. Using the two extremes or the ratio $[HIn]/[In^-]$, it follows from equation (15.50) that the minimum pH at which the colour of the indicator is perceptible is given by

$$pH = pK_{I_n} + \log \frac{1}{10} = pK_{I_n} - 1$$

which means that if pH is less than pK_{I_n} by unity, the indicator shows acidic colour and the maximum pH by

$$pH = pK_{I_n} + \log \frac{10}{1} = pK_{I_n} + 1$$

which means that if pH is greater than pK_{I_n} by unity, the indicator shows alkaline colour.

The indicator is changing colour in between these two extremes. Thus the useful range of any indicator is restricted to $pH = pK_{I_n} \pm 1$. For a particular titration, that indicator is chosen which has

$pK_{I_n} \approx pH$ at the end point because this indicator will exhibit colour change close to the end point.

A list of some common indicators and their colours together with their exponent values and pH ranges in which the colours show effective changes, is given in Table 15.5.

TABLE 15.5

Indicator	*Colours*		pK_{I_n}	*pH range*
	Acid	*Alkaline*		
Thymol blue	Red	Yellow	1.51	1.2--2.8
Methyl Orange	Red	Yellow	3.7	3.2—4.5
Bromophenol Blue	Yellow	Blue	3.98	3.0—4.6
Methyl Red	Red	Yellow	5.1	4.2—6.3
Chlorophenol Red	Yellow	Red	5.98	4.8 - 6.4
Bromocresol Purple	Yellow	Purple	6.3	5.2—6.8
Phenol Red	Yellow	Red	7.9	6.8—8.4
Cresol Red	Yellow	Red	8.3	7.2 – 8.8
Phenolphthalein	Colourless	Red	9.4	8.3 – 10.0
Thymolphthalein	Colourless	Blue	9.4	9.2—10.6

In addition to these individual indicators, sometimes a mixture of four or five more indicators, known as *Universal Indicators*, are used to cover pH range from 4 to 11. An important example of this type of Universal Indicator is a mixture of methyl red, α-naphtholphthalein, thymolphthalein, phenolphthalein and bromothymol blue. This covers pH range from 4 to 11 and gives a definite colour at different pH values as shown below:

pH	4	5	5	7	8	9	10	11
Colour	Red	Orange-Red	Yellow	Green-Yellow	Green	Blue-Green	Blue-Violet	Red-Violet

Calcultaion of pH of solutions by indicators. This can be very conveniently done by using Equation (15.50). The pH of the solution is first determined approximately by the use of Universal Indicator. This gives a clue for choosing the best indictor. This indicator is then added to a certain volume of the solution to be tested and the colour produced is compared with a series of solutions of known pH containing the same amount of the indicator. Thus by matching the colours, the pH of the solution can be determined within the accuracy of the experiment.

Problem 15.8. The dissociation constant of Bromocresol purple indicator is 3.981×10^{-7} at 20°C. The indicator when added to a buffer solution gave colour which matched with 60 per cent basic colour and 8.8 per cent acidic colour. Find the pH of the buffer solution.

Solution.

$$pH = pK_{In} + \log \frac{[In^-]}{[HIn]}$$

or $$=\mathrm{p}K_{\mathrm{In}} + \log \frac{\text{Basic colour}}{\text{Acidic colour}}$$

Here, $\mathrm{p}K_{\mathrm{In}} = -\log K_{\mathrm{In}} = -\log 3.981 \times 10^{-7} = 6.40$

Basic Colour=60 per cent, Acidic Colour=8.8 per cent.

$$\mathrm{pH} = 6.40 + \log \frac{60}{8.8}$$

$$= 6.40 + 1.8336 = 8.2336.$$

The use of indicators in titration of acids and bases In acid-base titrations, use is made of the fact that the pH of a solution being titrated changes rapidly at the equivalence point. Thus when a curve between the pH of a solution and the volume of each addition of titrant is plotted, there will be greatest slope at the equivalence point. As discussed in the above section, *the choice of an indicator is determined by the pH of the solution at the equivalence point i.e., the indicator for which* $pH \approx \mathrm{p}K_{\mathrm{In}}$.

Type 1. Titration of strong acids and strong bases. In the titration of strong acids, and strong bases, such as HCl *vs.* NaOH, the pH at the point of exact equivalence is 7. Before the equivalence point, the pH of the solution is below 4. The addition of alkali from the burette will merely decrease the concentration of the acid and the curve will show a small pH rise. At the equivalence point, the curve becomes almost vertical due to a large change in pH *i.e.*, from 4 to 10. This large change in pH, which is from 4 to 10, is brought about by the existence of as small as 0.1 ml of the alkali in excess.

In such titrations, an indicator which changes colour in the pH range 4 to 10 is suitable. As can be seen from the table given above, methyl orange or phenolphthalein is the most suitable indicator in the titration of strong acids and strong bases. Generally phenolphthalein is preferred because in this case, the colour change is most conveniently detected.

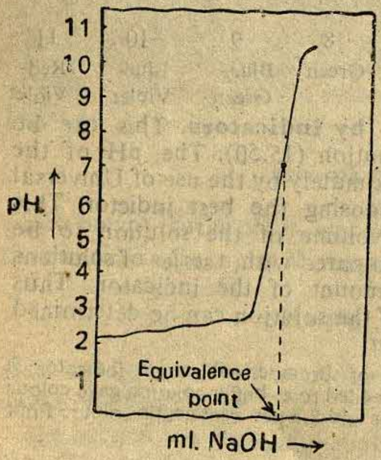


Fig. 15.1. Titration curve for strong acid HCl *vs* strong base NaOH.

Type 2. Titration of weak acids and strong bases. In the titration of a weak acid such as acetic acid by a strong base such as sodium hydroxide, the inflection of the curve is not so sharp as in type 1. This is due to the hydrolysis of the salt (sodium acetate) formed by the neutralization of acetic acid by sodium hydroxide at the equivalence point. At this point, the salt hydrolyses to give an alkaline solution and the pH value of the solution is nearly found to be 9. After the equivalence point, the hydrolysis of acetate ion becomes very small and the pH is determined only by sodium hydroxide added. Thus the slope near the equivalence point is much less steep *i.e.*, the pH changes less rapidly for a given amount of the base added than it does for the first type of curve.

In such titrations, an indicator which changes colour in the pH range 8-10 is most suitable. Thus, for such titrations, phenolphthalein is found to be the most suitable indicator.

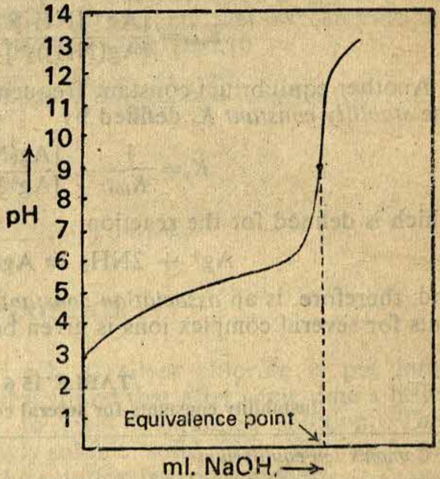


Fig. 15.2. Titration curve for weak acid (CH_3COOH) *vs* strong base (NaOH).

Type 3. Titration of strong acids and weak bases. Again in the titration of strong acids such as HCl and weak bases such as NH_4OH, the inflection of the curve is not sharp due to the hydrolysis of the salt. Since the acid is strong, the equivalence point will be on the acid side. In such titrations, an indicator which changes colour in the pH range 3 to 5 is most suitable. For this range, methyl orange is found to be the most suitable indicator.

Type 4. Titration of weak acids and weak bases. In the titration of weak acids such as acetic acid and weak bases such as NH_4OH, the pH range at the equivalence point is 6.5 to 7.5 and the curve shows little inflection. For such titrations, there is no suitable indicator although phenol red can be occasionally used. Hence in the titration of weak acids and weak bases, end point cannot be determined with accuracy and such types of titrations are generally avoided.

15.11. COMPLEX ION EQUILIBRIA (INSTABILITY CONSTANT)

A complex ion may be defined as an ion composed of several parts, each of which has some independent existence in solution as an ion, molecule or atom. SO_4^{2-} cannot be counted as a complex ion, because S^{6+} and O^{2-}, or other such pairs, do not exist in aqueous solution. In general terms, a complex ion consists of a substance (which may be uncharged molecules or negative ions), called a *ligand* and a metal ion *M* (usually a transition metal). The formula of the complex ion is *MLn*, where *n* is generally 2, 4 or 6. Some examples of complex ions are $Ag(NH_3)_2^+$, $Ag(CN)_2^-$, $Ag(S_2O_3)_2^{3-}$, $Cu(NH_3)_4^{2+}$, $Fe(CN)_6^{4-}$, $Fe(OH)^{2+}$, and $Zn(OH)_4^{2-}$.

The complex ion behaves as a weak electrolyte and dissociates to a small degree according to the equilibrium reaction:

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$$

The equilibrium constant for this reaction is the dissociation or ionization constant for the complex ion and is frequently referred to as the instability constant K_{ins} of the complex ion,

$$K_{ins}=\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} \qquad \ldots (15.51)$$

Another equilibrium constant frequently used for complex ions is the *stability constant* K_s defined by

$$K_s=\frac{1}{K_{ins}}=\frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} \qquad \ldots (15.52)$$

which is defined for the reaction

$$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$$

and, therefore. is an *association constant* A list of instability constants for several complex ions is given below in Table 15.6.

TABLE 15.6

Instability constants for several complex ions at 25°C

Complex ion equilibrium		K_{ins}
$[Cd(CN)_4]^{2-}$	$\rightleftharpoons Cd^{2+}+4CN^{1-}$	7.8×10^{-18}
$[Cd(NH_3)_4]^{2+}$	$\rightleftharpoons Cd^{2+}+4NH_3$	1.9×10^{-7}
$[Ag(NH_3)_2]^+$	$\rightleftharpoons Ag^++2NH_3$	6.3×10^{-8}
$[Ag(CN)_2]^{1-}$	$\rightleftharpoons Ag^++2CN^{1-}$	1.0×10^{-20}
$[Hg\,I_4]^{2-}$	$\rightleftharpoons Hg^{2+}+4I^{1-}$	5.3×10^{-31}
$[Hg(CN_4]^{2-}$	$\rightleftharpoons Hg^{2+}+4CN^-$	3.0×10^{-42}

In actual practice, the dissociation of a complex ion, like the ionization of a polybasic acid, occurs in steps as shown below:

1st step. $Ag(NH_3)_2^+ \rightleftharpoons Ag(NH_3)^+ + NH_3$

$$K_1=\frac{[Ag(NH_3)^+][NH_3]}{[Ag(NH_3)_2^+]}$$

2nd step. $Ag(NH_3)^+ \rightleftharpoons Ag^+ + NH_3$

$$K_2=\frac{[Ag^+][NH_3]}{[Ag(NH_3)^+]}$$

The constant calculated above is $K_{ins}=K_1.K_2$. In order to solve problems involving complex ions, one must know the equilibrium constants for the different ionization steps.

Problem. 15.9. Calculate the degree of dissociation of $Ag(NH_3)_2^+$ if $[Ag(NH_3)_2^+]$ is 0.10 M and $K_{ins}=6.3\times10^{-8}$.

Solution. The reaction involved is

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$$

$$K_{ins}=\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]}$$

It is evident from the reaction that

$$[Ag^+]=\tfrac{1}{2}[NH_3] \text{ or } 2[Ag^+]=[NH_3]$$

Also, $[Ag(NH_3)_2^+]=0.10-[Ag^+]$

Since the complex ion dissociates to a small extent, as is evident from the small value of the instability constant, then we can use the approximation that $[Ag(NH_3)_2^+]=0.10-[Ag^+]\simeq0.10$

Therefore $K_{ins}=\dfrac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]}=\dfrac{[Ag^+](2[Ag^+])^2}{0.10}=6.3\times10^{-8}$

Or $[Ag^+]=1.2\times10^{-3}$ M

The degree of dissociation is

$$\frac{[Ag^+]}{[Ag(NH_3)_2^+]}=\frac{1.2\times10^{-3}}{0.10}=1.2\times10^{-4}$$

15.12. THE SOLUBILITY PRODUCT

When a sparingly soluble salt, such as silver chloride is put into water and vigorously shaken, it is found that after some time a little of the salt dissolves in water to give a saturated solution. The equilibrium between the sparingly soluble solid ionic salt such as silver chloride and its ions in the solution is represented as

$$\underset{\text{(Solid)}}{AgCl} \rightleftharpoons \underset{\text{(in solution)}}{AgCl} \rightleftharpoons Ag^+ + Cl^-$$

Applying the law of Mass Action, the equilibrium constant is given by

$$K=\frac{[Ag^+][Cl^-]}{[AgCl]} \qquad \ldots (15.53)$$

But, since the unionised silver chloride is in contact with the solid silver chloride whose active mass is indeed constant, the concentration (more correctly activity) of unionised silver chloride can be taken constant. Therefore, equation (15.53) reduces to

$$K_{sp}=[Ag^+][Cl^-] \qquad \ldots (15.54)$$

The constant K_{sp} is referred to as the *solubility product constant* or simply the *solubility product* of silver chloride. In general, for any sparingly soluble electrolyte represented by AB, in contact with its saturated solution, the equilibria is represented by

$$\underset{\text{(Solid)}}{AB} \rightleftharpoons \underset{\text{(in solution)}}{AB} \rightleftharpoons A^+ + B^-$$

and the general expression for the solubility product is

$$K_{sp}=[A^+][B^-]$$

This expression is the basis of the solubility product principle which states that *in any solution saturated with sparingly soluble ionic salt, the product of the concentrations* (*more correctly activities*) *of its ions is a constant equal to solubility product.*

In case, the salt yields more than two ions, then the solubility product is given by the product of the concentrations of ions raised to a power equal to the number of ions produced by one molecule. Thus, for the salt, A_xB_y, the equilibrium is represented by

$$\underset{\text{(Solid)}}{A_xB_y} \rightleftharpoons \underset{\text{(Solution)}}{A_xB_y} \rightleftharpoons xA^+ + yB^-$$

and the expression for the solubility product is

$$K_{sp}=[A^+]^x\,[B^-]^y$$

Solubility and solubility product must not be confused with each other. The solubility of a salt is the quantity present in a unit amount of a saturated solution, expressed in moles per litre, grams per 100 ml, or other units. The solubility depends on what else is in the solution. On the other hand, solubility product, being an equilibrium constant, depends on the temperature and the nature of the salt. There is a connection, of course, between the solubility and the solubility product; if one is known, the other can be calculated. It should be noted further that the solubility product principle is valid only for sparingly soluble salts. Again, since the ionic product is equal to the solubility product only when the solution is saturated, this can be used to decide whether the precipitation is possible or not. If the product of concentrations of ions is smaller than the solubility product, the solution is unsaturated and no precipitation is possible. On the other hand, if the ionic product is larger than the solubility product, the solution is supersaturated and precipitation is possible.

Thus in the gravimetric estimation of Ba^{2+}, it is precipitated as $BaSO_4$ as its solubility product is very small. On the other hand, Ca^{2+} cannot be estimated by precipitating it as $CaSO_4$ because the solubility product of $CaSO_4$ is comparatively high. In general, lower is the K_{sp}, more insoluble is the salt.

Problem 15.10. The solubility product of $BaCrO_4$ is 2.0×10^{-10} at 25°C. Calculate the molarity of the $BaCrO_4$ solution.

Solution. $BaCrO_4$, being a sparingly soluble salt, dissociates as

$$BaCrO_4 \rightleftharpoons Ba^{2+} + CrO_4^{2-}$$

$$K_{sp}=[Ba^{2+}][CrO_4^{2}]$$

Let x g mole be the solubility of $BaCrO_4$ per litre. Then,

$$[Ba^{2+}]=[CrO_4^{2+}]=x \text{ g ion/litre}$$

$$2.0\times10^{-10}=x\times x=x^2$$

or $$x=\sqrt{2.0\times10^{-10}}=1.415\times10^{-5} \text{ g mol/litre}$$

Hence the molarity of this solution is 1.415×10^{-5} g mol/litre

PROBLEMS

1. What is meant by the dissociation constant of an acid? How can you measure the same for acetic acid? Can the same treatment be applied to HCl?

2. (*a*) Trace the development of Arrhenius theory of electrolytic dissociation. Point out its limitations.

(*b*) (*i*) Would an aqueous solution of H_2S be considered acidic according to the Arrhenius theory? Why?

(*ii*) Would gaseous HCl be considered an Arrhenius acid? Why?

(*iii*) Ammonia gas also dissolves in diethyl ether; would an ether solution of ammonia be considered basic in Arrhenius sense? Why?

3. State and explain Ostwald's dilution law. What are its limitations?

(*a*) What concentration of acetic acid is needed to give a $[H^+]$ of 3.5×10^{-4} mole $litre^{-1}$. $K_a = 1.8 \times 10^{-5}$. **Ans.** 7.1×10^{-3} mol/l

4. Strong acids dissociate nearly completely in aqueous solutions and the equilibrium constant is very large. Weak acids on the other hand only partially dissociate in water. Which acid, hydrogen fluoride or hydrogen cyanide, is the weaker acid? Given that $K_{HCN} = 4.0 \times 10^{-10}$ mol/litre and $K_{HF} = 6.9 \times 10^{-4}$ mole/litre.

5. What is the modern concept of an acid and a base? Explain with examples.

(*b*) Classify the following lewis acids and lewis bases:

SO_2, NH_3, I^-, Cr^{3+}, ether.

6. Acetic acid dissociates according to the equation:

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

a solution of acetic acid with initial concentration of 0.1 mol/litre was found to be 1 per cent dissociated. What is the equilibrium constant?

Ans. $K_{eq} = 1 \times 10^{-5}$ mol/litre

7. (*a*) Explain the term 'ionization constant' of water. How can you determine it experimentally?

(*b*) The degree of hydrolysis of potassium cyanide in N/100 solution was found to be 2.77×10^{-2}. If the dissociation constant of hydrocyanic acid is 1.3×10^{-9}, calculate the ionic product of water. **Ans.** 0.997×10^{-14}

8. What do you understand by the pH of a solution? What are buffer solutions? Calculate the pH of a solution containing 2 g of NaOH per litre of water. **Ans.** 12.7

9. What is meant by the term 'Degree of Hydrolysis' and 'Hydrolysis constant'? Deduce, in the case of a salt of a strong acid and a weak base, the relation between the hydrolysis constant and the dissociation constant of the base. How would you determine the degree of hydrolysis of aniline hydrochloride solution?

10. The acid ionization (hydrolysis) constant of Zn^{2+} is 2.2×10^{-10} (*a*) Calculate the pH of a 0.0010 F solution of $ZnCl_2$. (*b*) What is the basic dissociation constant of $Zn(OH^+)$? **Ans.** (*a*) +6.3 (*b*) 4.5×10^{-5}

11. Calculate the degree of hydrolysis and hydrolysis constant of a decinormal solution of NaCN, taking the ionization constant of water to be 1×10^{-14} and dissociation constant for HCN at 25°C is 7.2×10^{-10}.

Ans. 1.79×10^{-2} ; 1.36×10^{-5}

12. A solution of a weak acid such as HAc and a salt of the acid (NaAc) is called a *buffer*. Such solutions tend to resist the change in $[H^+]$. A buffer is made from HAc ($K = 1.9 \times 10^{-5}$ mole/litre) and NaAc. What must be the ratio, $[Ac^-]/[HA_c]$ in order that $[H^+]$ be equal to 4.0×10^{-5} M? **Ans.** 0-48

13. A buffer solution of pH 8.50 is desired (*a*) starting with 0.01 g formula weight of KCN and the usual inorganic reagents of the laboratory. how would you prepare one litre of the buffer solution? K_a for HCN is 4.1×10^{-10}.

(*b*) How much would the pH change after the addition of 5×10^{-5} mole NaOH to 100 ml of the buffer. **Ans.** Dissolve 0.01 gfw. KCN and 0.0087 mol HCN in one litre water (*b*) 0.19 units.

14. Define an acid-base indicator. What is the mechanism of their action? What is meant by the useful range of an indicator? Show with a rough graphical sketch how to choose an indicator for the titration of a weak acid with a strong base.

15. What do you understand by the term 'Solubility Product'? Discuss its applications in the separation of copper, zinc and magnesium from the mixture of their salts.

16. The solubility of Ag_2CrO_4 in water is 0·024 g/litre. Determine its solubility product.

17. How much NH_3 must be added to a 0.004 M Ag^+ solution to prevent the precipitation of AgCl when $[Cl^-]$ reaches 0.001 M? K_{sp} for AgCl is 1.8×10^{-10} and K for $Ag(NH_3)_2^+$ is 5.9×10^{-8}. **Ans.** 0.044 mol/litre

18. A solution is 0.010 M in cuprous ion (Cu^+) and 0.0010 M in lead ion (Pb^{2+}). Chloride ion is slowly added:

Will $PbCl_2$ ($K_{sp} = 1.6 \times 10^{-5}$ mol^3/l^3)

or CuCl ($K_{sp} = 3.2 \times 10^{-7}$ mole/l^2)

precipitate first? Show why.

Ans. CuCl would precipitate first as $[Cl^-]$ of 3.2×10^{-5}M is reached before $[Cl^-]$ of 1.3×10^{-1}M

19. What indicators will be suitable for the following titrations:

(*a*) HCl vs NaOH (*b*) $Ba(OH)_2$ vs H_2SO_4
(*c*) H_3BO_3 vs NaOH (*d*) HCOOH vs NaOH
(*e*) H_3PO_4 vs $Ba(OH)_2$

20. Write short notes on the following:

(*a*) Common ion effect (*b*) Buffer solution
(*c*) Levelling effect (*d*) Lewis concept of acids and bases

21. How would you explain the following:

(*a*) When NaCN is added to water, the resulting solution is basic.
(*b*) H_2S is a weak acid, yet it precipitates CuS from a solution of $CuSO_4$.
(*c*) $MgSO_4$ gives precipitate with NH_4OH but not with NH_4OH and NH_4Cl.
(*d*) H_3PO_2 is a mono-basic acid and H_3PO_4 is a tribasic acid.
(*e*) $NaHCO_3$ is alkaline to litmus but neutral to phenolphthalein.

Chapter 16

ELECTRO-CHEMICAL CELLS

16.1. INTRODUCTION

Take a commercial dry cell and connect its two terminals to a small motor. The motor starts functioning. This is due to the flow of electrons through the motor from the negative to the positive terminal of the cell. This electric current which causes the motor to work is due to chemical reaction occurring inside the cell. Thus, a device which produces electrical work at the expense of some physico-chemical process going on inside it, is called a *electro-chemical* or a *galvanic cell* and the chemical reaction occurring inside the cell is called the *cell reaction*. Electrochemical cells may be used to perform two functions (*i*) to convert chemical energy into electrical energy, and (*ii*) to convert electrical energy into chemical. In the dry cell considered above and the lead storage battery chemical energy is converted into electrical energy, while in the charging of a storage battery, chemical energy is converted into electrical. A cell is a single arrangement of two electrodes and an electrolyte capable of yielding electricity due to chemical action within the cell, or of producing chemical action due to passage of electricity through the cell. A battery, on the other hand, is a combination of two or more cells arranged in series or parallel. Thus, the ordinary 6-volt lead storage battery is a combination of three 2-volt cells connected in series.

The potential difference which exists between the two electrodes of a cell with open circuit is called *electromotive force*, or EMF of the cell and is expressed in volts. To illustrate this, take a Daniell cell (Fig. 16.1) which consists of two electrodes, one zinc and the other of copper, dipped into $ZnSO_4$ and $CuSO_4$ solutions respectively. The two solutions are separated by a porous partition. The zinc sulphate solution contains Zn^{2+} ions and so when metallic zinc is placed in contact with it, a definite equilibrium is set up between the metal and the ions of zinc, as

$$Zn^{2+}+2e \rightleftharpoons Zn \qquad \ldots (16.1)$$

where *e* represents electron. The conductivity is due to these electrons present in the solid. Similarly, a definite electron pressure is created at the interface between the copper and $CuSO_4$ solution, owing to the establishment of the equilibrium

$$Cu^{++}+2e \rightleftharpoons Cu \qquad \ldots (16.2)$$

On connecting these electrodes externally with a piece of wire, a steady steam of electrons flows through this conductor from zinc to copper. The direction of flow of electrons is so due to higher electron pressure of zinc than that of copper electrode. This flow of electrons causes more ionization in zinc and more copper is deposited, with the net effect that a chemical reaction has taken place by the passage of current. This is represented as follows :

$$Cu^{++} + Zn \rightleftharpoons Cu + Zn^{++} \qquad \ldots (16.3)$$

The zinc electrode is stamped with a minus sign and the copper electrode with a plus sign.

The above cell (Daniell) can be represented diagramatically as in Fig. 16.2.

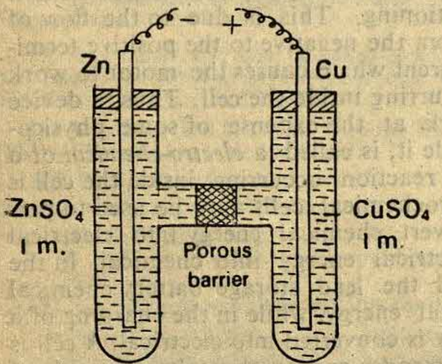


Fig. 16.1. A typical electro-chemical cell.

$$Zn \mid Zn^{++} \parallel Cu^{++} \mid Cu$$

$$\xrightarrow{\qquad\qquad}$$

Positive Current

Fig. 16.2. Diagrammatic representation of a cell.

16.2. MEASUREMENT OF E.M.F. USING POTENTIOMETER

The cell E.M.F. can be measured with the help of a potentiometer. This involves the balancing of the E.M.F. of an electro-chemical cell against an equal and opposite-potential difference in the slide wire of a potentiometer. The schematic diagram is shown in Fig. 16.3.

It consists of a storage battery B', the constant E.M.F. of the storage battery must be larger than that of the cell under measurement. This sends a current i_B through the slide wire AB. The cell to be studied is also connected to A having the +ve pole in the same direction as the strorage battery B' and sends current in the same direction. The sliding contact D can be adjusted until the galvanometer G shows zero deflection. This is called the *null point*. At this point the E.M.F. of the cell is balanced by the potential difference between the point A and D of the potentiometer wire. This slide wire is calibrated in terms of the fall of potential so that one can read potential drop across the wire directly. The fall of potential between *A* and *D* is equal to the E.M.F. of the unknown cell.

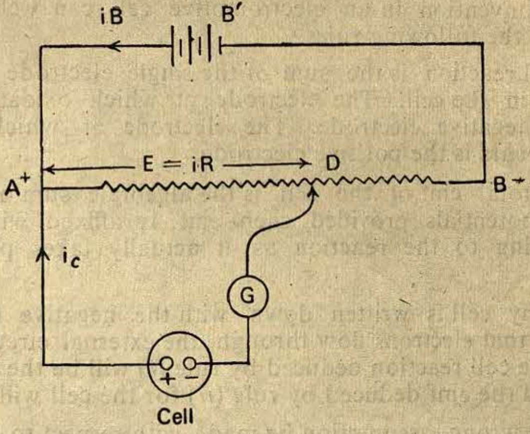


Fig. 16.3. Measurement of E.M.F. of a cell.

Thus one can easily find the E.M.F. of an unknown cell, provided the E.M.F. of the storage battery is more than that of the cell under test.

(If E_t is the E.M.F. of a cell with transference number t and E is the E.M.F. of the same cell, *i.e.*, with the same end electrodes and with the same solutions, without transference, we have the relation

$$\frac{E_t}{E}=t$$

i.e., the transference number of the anion is determined by the ratio of the E.M.F.s of the two concentration cells one with transference and the other without transference.)

In studying cells it is necessary to determine not only the e.m.f. of the cell but also the reaction responsible for it. The nature of the reaction proceeding in a cell can be deduced from the manner in which the electrodes must be connected to the standard cell in order to obtain a balance of the potentiometer. Such a balance is possible when the electrode connected to the negative side of the cell is the negative electrode, while the one connected to the positive side is the positive electrode. Further since a negative electrode contains electrons in excess of the number present on the positive electrode, the electrons will flow from the negative to the positive electrode in the external circuit. Hence oxidation must occur at the negative electrode where electrons are given off and reduction must take place at the positive electrode.

16.3. SIGN CONVENTIONS

The sign convention in an electromotive cell can well be understood from the following rules :

(*i*) A cell reaction is the sum of the single electrode reactions as they occur in the cell. The electrode at which oxidation reaction occurs is negative electrode. The electrode at which reduction reaction occurs is the positive electrode.

(*ii*) The total emf of the cell is the algebraic sum of the single electrode potentials provided each emf is affixed with the sign corresponding to the reaction as it actually takes place at the electrode.

(*iii*) If any cell is written down with the negative electrode on the left, so that electrons flow through the external circuit from left to right, the cell reaction deduced by rule (*i*) will be the spontaneous process and the emf deduced by rule (*ii*) for the cell will be positive.

(*v*) If the wrong assumption be made with respect to the polarity of the electrodes, rule (*iii*) will give a negative emf corresponding to the non-spontaneous reaction. To obtain the spontaneous reaction and its emf, all that need be done is to be reverse the reaction and change the sign of the emf without changing its magnitude.

Let us summarise the conventions about cells in the form of rules.

(*i*) Solid lines or semicolon represent interfaces between solutions and solid electrodes.

(*ii*) Vertical broken lines represent salt bridge, porous partition, or other junction between two half-cells.

(*iii*) The sign given to the emf indicates the polarity of the right hand electrode.

(*iv*) The least oxidised species in each half are written next to the solid electrode. For example, H^+. MnO_4^- Mn^{2+}/Pt and Pt/Fe^{2+}, Fe^{3+}·

(*v*) The sign of a given standard electrode potential is that assigned to the cell formed by the standard electrode and the standard hydrogen electrode when the latter is written to on the left hand side of the cell diagram.

The following examples will help in better understanding of these values and the way in which a cell reaction is associated with a given cell.

(*i*) $A;A^+ \parallel B^+;B$

$$E = E_{A;A^+} + E_{B^+;E}$$

Oxidation $A = A^+ + e$

Reduction $B^+ + e = B$

Cell reaction $A + B^+ \rightleftharpoons A^+ + B$

(*ii*) $B;B^+ \| A^+;A$

$E=E_{B;B^+}+E_{A^+;A}$

Oxidation $B \rightleftharpoons B^+ + e$

Reduction $A^+ + e = A$

Cell reaction $B + A^+ = B^+ + A$

(*iii*) $A;\ A^+ \| \bar{C}\ ;C$

$E=E_{A:A^+}+E_{C^-;C}$

Oxidation $A = A^+ + e$

Reduction $C + e = C^-$

Cell reaction $A + C \rightleftharpoons A^+ + C^-$

16.4. REVERSIBLE ELECTRODE PROCESSES

The concept of reversibility as it applies to the processes which take place at the electrodes of a cell must now be discussed in more detail. During the working of a cell, there are normally chemical changes taking place at each electrode and associated with this is the gain of electrons at the cathode and the loss of electrons at the anode. In order to be reversible, the electrode materials must only take part in chemical changes which correlate exactly with the electrical changes. No energy or material must be transformed in any other way and a very small increase in the potential difference in the external circuit opposing that of the cell must exactly reverse the chemical changes. It will be recalled that the conditions for thermodynamic reversibility are (*i*) that the driving and opposing forces be only infinitesimally different from each other, and (*ii*) that it should be possible to reverse any change taking place by applying a force infinitesimally greater than the one acting. When these requirements are satisfied by a cell, the cell is reversible, and its potential difference measured under appropriate conditions may be substituted into the relevant thermodynamic relations. When these conditions are not satisfied, the cell is said to be irreversible and the thermodynamic equations do not apply.

16.5. NERNST EQUATION

Nernt equation correlates the cell E.M.F. to a standard value E° and the activities of the species taking part in the cell reaction. This can be discussed in the following steps:

For an electro-chemical cell, the reaction free energy ($\triangle G$) can be given by a relation:

$$\triangle G = -nEF \qquad \ldots (16.4)$$

where n is number of equivalents and F is a quantity of electricity, known as the Faraday constant. E is the E.M.F. of the cell.

Also, the free energy for any chemical reation can be expressed as

$$\triangle G=\triangle G^{\circ}+RT\, lnQ \qquad \ldots (16.5)$$

Here Q is the quotient of activities. In this case

$$Q=\frac{[\text{Reduced State}]}{[\text{Oxidised State}]} \qquad \ldots (16.6)$$

Now from (16.4) and (16.5) we have

$$-nFE=-nFE^{\circ}+RT\, lnQ$$

($\because$ $\triangle G^{\circ}=-nFE^{\circ}$, E° being the standard E.M.F. of the cell)

Dividing both sides of this equation by nF we get

$$-E=-E^{\circ}+\frac{RT}{nF}\, ln\, Q$$

or

$$E=E^{\circ}-\frac{RT}{nF}\, lnQ \qquad \ldots (16.7)$$

Substituting for Q from (16.6) in (16.7) we get,

$$E=E^{\circ}-\frac{RT}{nF}\, ln\frac{[\text{Reduced State}]}{[\text{Oxidised State}]}$$

or

$$E=E^{\circ}+\frac{RT}{nF}\, ln\frac{[\text{Oxidised State}]}{[\text{Reduced State}]} \qquad \ldots (16.8)$$

The equation (16.8) is known as the Nernst equation, and can be written in a number of forms as follows:

$$E=E^{\circ}+\frac{RT}{nF}\, ln\frac{[\text{Oxidised State}]}{[\text{Reduced State}]} \qquad \ldots (16.8a)$$

$$E=E^{\circ}+\frac{2.303\, RT}{nF}\, \log_{10}\frac{[\text{Oxidised State}]}{[\text{Reduced State}]} \qquad \ldots (16.8b)$$

For all practical purposes, R is 8.313 joules and F is 96,500 coulombs; at 25°C, $T=298$K. Inserting the value of these constants in (16.8b), we get

$$E=E^{\circ}+\frac{0.05915}{n}\, \log_{10}\frac{[\text{Oxidised State}]}{[\text{Reduced State}]} \qquad \ldots (16.8c)$$

For an electrode of metal M, which shows an equilibrium given below:

$$E=M^{n+}+ne\rightleftharpoons M$$

The above equation becomes

$$E=E^{\circ}+\frac{0.05915}{n}\, \log\, [M^{n+}]$$

and for anion electrode like

$$Cl+e\rightleftharpoons Cl^{-}$$

The Nernst equation will take the form

$$E=E^{\circ}+0.05915 \log \left[\frac{1}{\mathrm{Cl}^{-}}\right]$$

Electrode potentials vary with concentration and may even change sign. Thus we have two choices for calculations of cell potential.

(*a*) Calculate both single electrode potentials separately by application of the Nernst equation. Then designate the larger *E* value as that for the internal cathode, or

(*b*) Arbitrarily write the balanced net equation for the cell reaction as it would proceed spontaneously under standard state conditions. Calculate E_{cell} from the Nernst equation. If the calculated value of E_{cell} is negative, then the actual spontaneous reaction must be represented by the reverse of the equation originally written.

The standard electrode potentials of some important systems are given in Table 16.1.

The potential of an electrode may be expressed either as the *oxidation potential* (which measures the tendency of a half-reaction to occur, in the direction corresponding to oxidation) or *reduction potential* (representing the opposite tendency). The more *positive* the potential, the more the electrode tends to behave as an *anode*; the more *negative* the potential, the more it tends to be a *cathode*. The most positive potentials belong to the half-reactions in which the best reducing agents are oxidized, and their oxidized forms are the poorest oxidizing agents. For example, the potential +3.04 volts indicates that lithium is a very good reducing agent, because if is easily oxidised to Li^+ whereas it is very difficult to reduce Li^+ to Li, so that Li^+ is a poor oxidizing agent. Sodium, with an oxidation potential of +2.71 volts, is also a good reducing agent, but not quite so good as Li. At the other extreme, the potential for the half-reaction $2F^- \rightleftharpoons F_2 + 2e^-$ is −2.85 volts, which signifies that F^- is a very poor reducing agent, being oxidized to F_2 only with great difficulty; conversely, F_2 is the best of all oxidizing agents.

The results obtained for the *standard electrode potentials* of a number of electrodes at 25°C are given.

Problem 16.1. Calculate the equilibrium constant at 25°C for the reaction

$$Zn(s)+Cu^{2+}\ (1\ m) \rightleftharpoons Cu(s)+Zn^{2+}\ (1\ m)$$

E° for this cell is 1.10V

Solution. $\Delta G^{\circ}=-nFE^{\circ}=-2.303\ RT \log K$

Then $\log K=\dfrac{nFE^{\circ}}{2.303\ RT}$

$$=\frac{2\times96485\times1.10}{2.303\times8.314\times298}$$

$$=37.2$$

$K=1.6\times10^{37}$ **Ans.**

TABLE 16.1
Standard reduction (electrode) potentials

	Half reaction	$E^\circ(V)$	
Very weak Oxiding agent	$Li^++e^-\rightarrow Li$	-3.04	Very strong reducing agents
	$Cs^++e^-\rightarrow Cs$	-2.95	
	$Rb^++e^-\rightarrow Rb$	-2.93	
	$K^++e^-\rightarrow K$	-2.92	
	$Ba^{2+}+2e^-\rightarrow Ba$	-2.90	
	$Sr^{2+}+2e^-\rightarrow Sr$	-2.89	
	$Ca^{2+}+2e^-\rightarrow Ca$	-2.87	
	$Na^++e^-\rightarrow Na$	-2.71	
	$Mg^{2+}+2e^-\rightarrow Mg$	-2.37	
	$Al^{3+}+3e^-\rightarrow Al$	-1.66	
	$Mn^{2+}+2e^-\rightarrow Mn$	-1.18	
	$2H_2O+2e^-\rightarrow H_2(g)+2OH^-$	-0.83	
	$Zn^{2+}+2e^-\rightarrow Zn$	-0.76	
	$Cr^{3+}+3e^-\rightarrow Cr$	-0.74	
	$Fe^{2+}+2e^-\rightarrow Fe$	-0.44	
↑ Oxiding strength decreasing	$Cr^{3+}+e^-\rightarrow Cr^{2+}$	-0.41	reducing strength decreasing ↓
	$Co^{2+}+2e^-\rightarrow Co$	-0.28	
	$Ni^{2+}+2e^-\rightarrow Ni$	-0.25	
	$Sn^{2+}+2e^-\rightarrow Sn$	-0.14	
	$Pb^{2+}+2e^-\rightarrow Pb$	-0.13	
	$2H^{2+}+2e^-\rightarrow H_2$	-0.00	
	$Sn^{4+}+2e^-\rightarrow Sn^{2+}$	$+0.15$	
	$Cu^{2+}+2e^-\rightarrow Cu$	$+0.34$	
	$Cu^++e^-\rightarrow Cu$	$+0.52$	
	$I_2+2e^-\rightarrow 2I^-$	$+0.54$	
	$O_2+2H^++2e^-\rightarrow H_2O_2$	$+0.68$	
	$Fe^{3+}+e^-\rightarrow Fe^{3+}$	$+0.77$	
	$NO_3^-+2H^++e^-\rightarrow NO_2(g)+H_2O$	$+0.78$	
	$Ag^++e^-\rightarrow Ag$	$+0.80$	
	$NO_3^-+4H^++3e^-\rightarrow NO+H_2O$	$+0.96$	
	$Br_2+2e^-\rightarrow 2Br^-$	$+1.07$	
	$\frac{1}{2}O_2+2H^++2e^-\rightarrow H_2O$	$+1.23$	
	$4H^++MnO_2+2e^-\rightarrow Mn^{2+}+2H_2O$	$+1.28$	
	$Cr_2O_7^{2-}+14H^++6e^-\rightarrow 2Cr^{3+}+7H_2O$	$+1.33$	
	$Cl_2+2e^-\rightarrow 2Cl^-$	$+1.36$	
	$Au^{3+}+3e^-\rightarrow Au$	$+1.50$	
	$MnO_4^-+8H^++5e^-\rightarrow Mn^{2+}+4H_2O$	$+1.52$	
Very strong oxidising agents	$H_2O_2+2H^++2e^-\rightarrow 2H_2O$	$+1.77$	Very weak reducing agents
	$F_2+2e^-\rightarrow 2F^-$	$+2.85$	

Problem 16.2. Calculate the single electrode potential for copper metal in contact with 0.10 M Cu^{2+} solution. E° for copper is 0.34 volt.

Solution. Reduction half reaction for copper can be written as,

$$Cu^{2+} + 2e^- \rightarrow Cu$$

$$E = E^\circ - \frac{0.0592}{n} \log Q$$

$$n = 2,\ E^\circ = +0.34 \text{ volt}$$

$$Q = \frac{1}{C_{Cu^{2+}}} = \frac{1}{0.10} = 10$$

$$\therefore \quad E = E^\circ - \frac{0.0592}{2} \log 10$$

$$= 0.34 - 0.0296$$

$$= 0.31\text{V} \qquad \textbf{Ans.}$$

16.6. NERNST THEORY OF ELECTRODE-POTENTIAL

The ultimate source of E.M.F. in a galvanic cell is the chemical reaction which proceeds when current is flowing through it. According to the theory, proposed by Nernst, all the metallic elements and hydrogen have a tendency to pass into solution in the form of +ve ions. This property of the metal is known as its *solution pressure*. Due to the migration of +ve ions, the metallic electrode is left negatively charged resulting in the formation of an electrical double layer at the electrode. If a metal electrode is dipped in a solution of one of its salts the situation becomes slightly different.

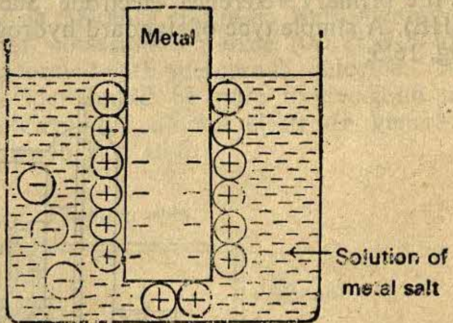


Fig. 16.4. Electrical double layer.

In such a case, the tendency of the metal to pass into solution as ions is opposed by the reverse tendency of the ions to get deposited back on to the electrode. This backward reaction is attributed to the *osmotic pressure* of the ions in solution. This is shown in Fig. 16.4.

The standard electrode potential of the metal is equal to the defference between its solution pressure and the osmotic pressure of its ions. In this case, two possibilities can arise:

(*i*) The solution pressure of the metal exceeds the osmotic pressure of its ions. Here the cations pass into solution more rapidly thus leaving the electrode negatively charged. The example is zinc rod dipped in zinc sulphate solution.

(*ii*) The solution pressure of the metal is less than the osmotic pressure of its ions. In this case the cations will be driven out of the solution and will get deposited on the electrodes making it positively charged. The example is provided by a copper electrode dipped in copper sulphate solution.

16.7. REFERENCE ELECTRODES

Now the question is, Is it possible to measure the single electrode potential directly. However, it can be measured indirectly by coupling the electrode whose single electrode potential is to be measured with a reference electrode. The choice of a reference electrode in a particular situation depends on the nature of the substance in solution. There are two types of reference electrodes:

1. Primary Reference Electrode, and
2. Secondary Reference Electrode.

Primary reference electrodes. A hydrogen electrode is used as the primary reference electrode Standard Hydrogen Electrode (SHE). A simple type of standard hydrogen electrode is shown in Fig. 16.5.

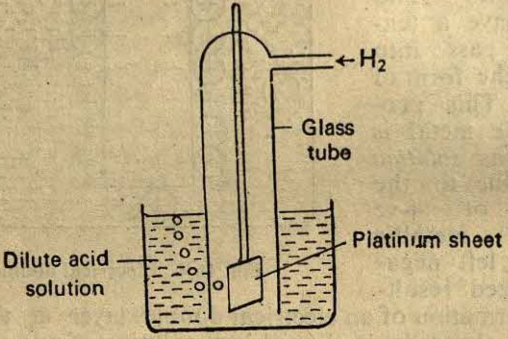


Fig. 16.5. Hydrogen electrode.

Purified hydrogen gas is passed through an acid solution. A platinum electrode coated with platinum black is dipped in the solution. As the hydrogen is in the gaseous form, this electrode acts as a charge carrier. The gas is bubbled out at the end of the tube as shown in the diagram. At the electrode surface the reversible reaction that takes place is:

$$H^{+}_{(aq)} + e^{-}\,(Pt) \rightleftharpoons \tfrac{1}{2}H_{2(g)} \qquad \ldots (16.9)$$

By convention, the hydrogen electrode is assigned the value $E^\circ = 0$ when the platinum electrode is dipped in a solution of HCl of mean activity $a = 1$ and the hydrogen gas is bubbled at 1 atm. pressure. It can be represented as

$$Pt/H_2\,(1\text{ atm.})/H^+\,(a=1) \qquad \ldots (16.10)$$

All other potentials expressed on this basis are referred to as potentials on the hydrogen scale.

In the hydrogen electrode, platinum is poisoned by the adsorbed impurities from the solution and this causes difficulty in its use as it checkes the reversibility of the reaction.

Secondary reference electrodes. In the use of hydrogen cell, many difficulties arise: such as the difficulty of setting up a hydrogen gas electrode, use of liquid junctions, etc. For the ake of simplicity, several secondary electrodes, whose potentials are known on the hydrogen scale, are used in place of hydrogen electrode. A number of electrodes are known and their use depends upon the substances in solution. It is always desirable to choose an electrode which will not require a salt bridge. One such electrode is the calomel electrode.

(*a*) **Calomel electrode.** For the solutions having a chloride ion, the calomel electrode is used as reference electrode. Here mercury is in contact with a solution of potassium chloride (0.1 N, 1 N and saturated solution of KCl) saturated with mercurous chloride. The mercury and mercurous chloride should be pure to give good and reproducible results. A simple type of calomel electrode generally used in the laboratory is shown in Fig. 16.6.

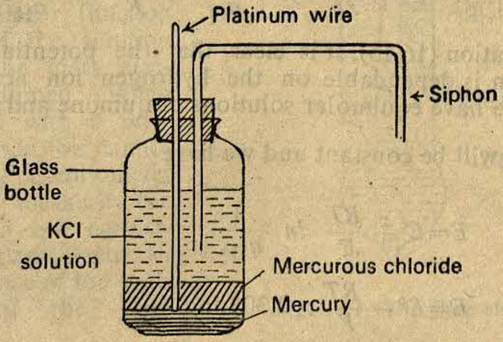


Fig. 16.6. Calomel Electrode.

It consists of glass vessel with small quantity of pure mercury at the bottom. The mercury layer is covered with paste of mercurous chloride and is filled with a saturated solution of KCl. A platinum wire is fused in glass tube and a siphon tube provides for the connection.

The half-cell reaction is:

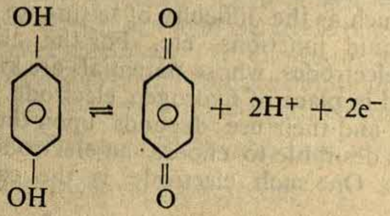
$$Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^- \qquad \ldots (16.11)$$

The potential of a calomel electrode at 25°C is given by:

$$E = 0.2676 - 0.05915 \log a_{Cl^-} \qquad \ldots (16.12)$$

In case the salt bridge is used with calomel electrode, then, its potential is fixed by the chloride ion concentration around it.

(*b*) **The quinhydrone electrode**. Organic compounds show a reversible oxidation-reduction system. A common example is provided by a mixture of quinone and hydroquinone, in presence of hydrogen ions. The system can be represented as:



. . . (16.13)

All such systems can be represented by a general equation.

According to Nernst equation, the potential of the system is given by

$$E=E^\circ+\frac{RT}{2F}\ ln\ \frac{a_{H_2Q}}{a_Q.a^2_{H^+}} \qquad \ldots (16.14)$$

$$E=E^\circ+\frac{RT}{2F}\ ln\ \frac{a_{H_2Q}}{a_Q}+\frac{RT}{F}\ ln\ \frac{1}{a_{H^+}} \qquad \ldots (16.15)$$

From equation (16.15), it is clear that the potential in quinhydrone system is dependable on the hydrogen ion activity of the system. If we have equimolar solutions of quinone and quinhydrone, then $\frac{a_Q}{a_{H_2Q}}$ will be constant and we have

$$E=E^\circ+\frac{RT}{F}\ ln\ \frac{1}{a_{H^+}}$$

or

$$E=E^\circ-\frac{RT}{F}\times 2.303 \log a_{H^+}$$

Since, $pH=-\log a_{H^+}$

The above equation becomes

$$E=E^\circ+\frac{RT}{F}\times 2.303\ pH$$

or

$$E=E^\circ+\frac{2.303\ RT}{F}pH \qquad \ldots (16.16)$$

The quinhydrone electrode has a gold wire dipped in a solution of unknown pH. The solution is made saturated with quinhydrone and this is combined with a suitable reference electrode. The buffer solution is used for calibration. The potential of this electrode is a linear function of pH only below pH 8.5. This is due to the oxidation of hydroquinone in alkaline solution.

Advantages and limitations. The quinhydrone electrode is extremely simple to set up, and it gives its true reversible potential immediately. It is applicable to many types of solution and gives pH values as accurately as the hydrogen electrode. It can sometimes be used in solutions containing reducible substances (*e.g.*, dil HNO_3, NO_3^-, Cu^{2+}, Pb^{2+}, Cd^{2+}, unsaturated acids where the hydrogen electrode is not applicable. Very small solutions are sufficient for substances using quinhydrone electrode. The electrode cannot be used with solutions containing any substances which might react with quinone or hydroquinone. The results obtained are inaccurate in solutions of pH more than 8.5. This is because hydroquinone begins to oxidise from the air.

(*c*) **Glass electrode**. It consists of a glass vessel of special design as shown in Fig. 16.7 and is filled with dil. HCl solution. A silver electrode coated with AgCl is immersed in the HCl solution. The lower part of the apparatus is blown very thin forming a glass membrane. The potential of a cell, having glass electrode, is a linear function of the pH of the solution in which the glass electrode is dipped. When this is used with a reference electrode, we cannot use ordinary potentiometer circuits to measure the E.M.F. of a cell consisting of a glass electrode. This is because of the high resistance of the glass membrane.

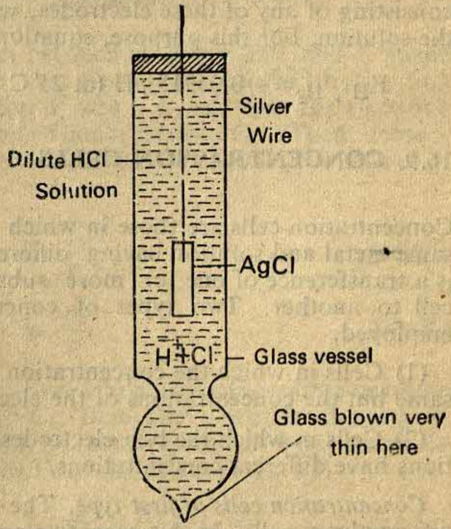


Fig. 16.7. The glass electrode.

To measure the potential difference, a vacuum tube voltmeter is frequently used. Its operation is similar to a concentration cell *i.e.*, the solutions outside and inside the glass membrane have different H^+ ion concentrations. Due to this, a potential difference, called the liquid junction potential or the diffussion potential, is set up. This potential difference depends upon the pH of the outer solution and can be expressed as

$$E = E' - \frac{2.303}{F} RT\,pH \qquad \ldots (16.17)$$

where E' is a constant, and depends on the reference electrode used. This is the most convenient method for the measurement of pH. No oxidising, reducing and other types of substances can affect the electrode. The calibration of the electrode is done against the standard buffer solutions. For use of the alkaline solutions, this must be made up of a special glass. The function of glass electrode is limited up to aqueous solutions only.

16.8. ELECTRODES FOR THE MEASUREMENTS OF pH

We have seen in the case of hydrogen electrode, quinhydrone electrode and glass electrode that these electrodes involve the equilibrium concentration of hydrogen ions and since the pH of a solution depends on the H^+ ion concentration (*i.e.*$-$pH$=\log [H^+]$) we can measure the pH of the solutions using these electrodes. Since the potential of an electrode which involves either H^+ or OH^- ions, depends on the pH of the solution, by measuring E.M.F. of the cell consisting of any of these electrodes, we can determine the pH of the solution. For this purpose, equation (16.16) can be written as:

$$E_{H^+,\, H_2} = -0.05915 \text{ pH (at } 25^\circ\text{C and } P = 1 \text{ atm)} \qquad \ldots (16.18)$$

16.9. CONCENTRATION CELLS

Concentration cells are those in which the cells are composed of the same metal and solution having different concentrations, and there is a transference of one or more substances from one part of the cell to another. Two types of concentration cells are generally employed.

(1) Cells in which the concentration of the two solutions are the same but the concentrations of the electrodes are different.

(2) Cells in which the two electrodes are identical but the solutions have different concentrations.

Concentration cells of first type. The example of this type of cells are amalgam cells. In this case, two amalgams of the same metal at two different concentrations are immersed in a solution containing the metal ions. Let us consider the two electrodes of zinc amalgam having the concentrations of zinc C_1 and C_2, dipped in a solution of zinc sulphate. This can be represented as:

$$\mathbf{Zn-Hg\ (C_1)\ |\ ZnSO_4\ aq.\ |\ Zn-Hg\ (C_2)}$$

The E.M.F. is, therefore, given by

$$E = \frac{RT}{nF} \ln \frac{C_2}{C_1} \qquad \ldots (16.19)$$

Actually speaking, the more rigorous thermodynamic quantity—the mean activity coefficient, should be used in place of concentration. However, in case of very dilute solutions, we can use concentration in place of activity. In this particular case, $n=2$. Similar cells can be made using Zn, Pb, Sn and Cu electrodes.

Concentration cells, of second type. In such cells the two electrodes of the same metal are dipped in two solutions with different concentrations of the metal ions. The general arrangement of such a cell is shown in Fig. 16.8.

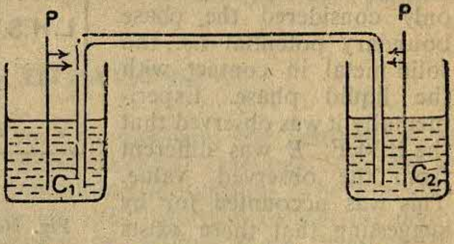


Fig. 16.8. Concentration cell of the second type.

It can be represented as: $\mathbf{M/M^+ (C_1) \;/\; M^+(C_2) \;/\; M}$ where $C_2 > C_1$. Let two similar metals (having the same solution pressure) p, be dipped in solutions of their ions of different concentrations C_1 and C_2. Let p_1 and p_2 be their respective osmotic pressures. The contact between these two half cells is made by an inverted tube. Let e_1 be the electrode potential in the first solution where the concentration of ions is C_1 and e_2 is the electrode potential of the second solution of concentration C_2. Then according to Nernst electrode potential equation, relations for e_1 and e_2 are given by

$$e_1=\frac{RT}{nF}\ ln\ \frac{p_1}{p} \qquad \ldots (16.20)$$

and

$$e_2=\frac{RT}{nF}\ ln\ \frac{p_2}{p} \qquad \ldots (16.21)$$

Here one electrode becomes +ve while the other becomes −ve relative to the first one. If $C_2>C_1$, then the electrode dipping in solution of concentration C_2 will be relatively more +ve electrode than the other. The actual E.M.F. of the cell is given by

$$E=e_2-e_1=\frac{RT}{nF}\ ln\ \frac{p_2}{p}-\frac{RT}{nF}\ ln\ \frac{p_1}{p} \qquad \ldots (16.22)$$

or

$$E=\frac{RT}{nF}\ ln\ \frac{p_2}{p}\times\frac{p}{p_1}$$

$$=\frac{RT}{nF}\ ln\ \frac{p_2}{p_1}$$

This can also be written as:

$$E=\frac{RT}{nF}\ ln\ \frac{C_2}{C_1} \qquad \ldots (16.23)$$

Thus E can be calculated. Here $p_2 \propto C_2$ only if we assume that the solutions are very dilute and obey the ideal solution laws. A typical cell of this type is shown in Fig. 16.9.

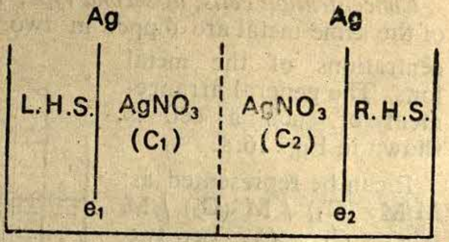


Fig. 16.9. A typical concentration cell.

In this derivation, we have only considered the phase boundary potential *i.e.*, the solid metal in contact with the liquid phase. Experimentally it was observed that the E.M.F. E was different from the observed value. This was accounted for by suggesting that there exists a potential known as the diffusion potential at the junction of the solutions. Hence a correction has to be made.

$$E = e_2 - e_1 \pm e_3 = RT \ln \frac{C_2}{C_1} \qquad \ldots (16.24)$$

where $\pm e_3$ is known as the liquid junction potential.

16.10. LIQUID JUNCTION POTENTIAL

It has been found that the experimental value of E.M.F. (E) for the cell of second type, discussed in the previous section, does not agree with the theoretically expected value. The reason for this difference can be seen as follows:

While calculating the E.M.F. E of this cell, we have assumed that the solution interface is the only seat of potential, though there is yet another surface of contact *i.e.* liquid-liquid contact. This gives rise to another potential called the *liquid-junction potential*. In cells where the two solutions of an electrolyte of different concentrations are brought in contact with one another, the more concentrated solution will tend to diffuse in the more dilute solution. Two cases will arise:

(*a*) When the cation moves faster than the anions, then the former will tend to diffuse ahead of the latter into the solution. Thus this solution will become positively charged with respect to the concentrated solution.

(*b*) When the anion moves faster than the cation, the dilute solution will acquire a negative charge.

In either case, "an electrical double layer" is produced at the junctions of the two layers. The attraction between the opposite charges will prevent any appreciable separation of anions from cations and this leads to the development of a potential difference at the boundary called the liquid junction potential or sometimes the diffusion potential.

However, when the speed of the moving ions are equal, the liquid junction potential becomes zero as in the case of solutions of KCl, NH_4Cl etc. It is for this reason that saturated solutions of these electrolytes are used as salt bridge, to avoid, the liquid junction potential.

16.11. POTENTIOMETER TITRATIONS

The branch of quantitative analysis involving the estimation of substances in solution by the measurement of potentials is known as potentiometric analysis or potentiometric titration. The potentiometric measurements provide us the facility of conducting many titrations. The essential condition to conduct these titrations is, that the reaction must involve the addition or removal of some ion for which an electrode is available.

The potential (E) of any form of hydrogen electrode, measured against any convenient reference electrode, is related to the pH of the solution by the equation,

$$E=E^\circ+\frac{RT}{F}pH \qquad \ldots (16.25)$$

where E° is the potential of the reference electrode and is constant. Thus pH measurements can also serve for potential-measurements (E).

In titrations involving acid-base neutralization, the potential (or pH) can be measured after successive additions of small volumes of the titrant. This change in potential (or pH) is plotted against the volume added, resulting in a S shaped curve as shown in Fig. 16.10. This curve is known as potentiometric titration-curve and has the greatest slope at the equivalence-point.

The addition of small amount of titrant at this point *i.e.*, end point, has a much greater effect upon the solution than elsewhere. Consider the titration involving hydrochloric acid and sodium hydroxide. Let a solution of NaOH be added to a solution of HCl. To minimise the volume-error, the acid should be 0.01 N and the normality of the base around 0.1 N.

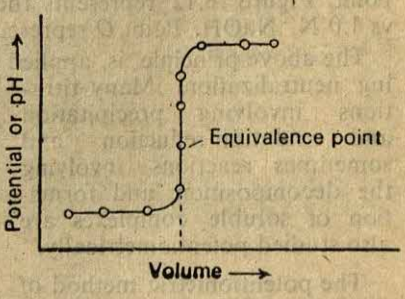


Fig. 16.10. Potentiometric titration curve.

After each addition, the emf is read. When the later begins to show a tendency to increase appreciably, the increments are made smaller and smaller until near the end point, only 0.1 cm^3 or less are added at a time. By such a procedure, it is possible to obtain a sharp maximum and hence with in narrow limits the volume of base equivalent to the acid taken On plotting a graph between change in potential and the volume of NaOH added, we get a curve shown in Fig. 16.10.

The above figure shows that the equivalence point corresponds to the steepest portion of the curve. If the solutions are dilute or either the base or acid is weakly ionized, the curve shows less steepness, thus, causing difficulty in obtaining a sharp-end point. In such cases, a differential curve is drawn which is a curve between $\triangle E/\triangle V$ and the volume added. $\triangle E/\triangle V$ is obtained with the help of original curve. The maximum value of $\triangle E/\triangle V$ corresponds to the end-point. Figure 16.12 represents the differential curve of 0.01 N HCl vs 1.0 N. NaOH. Point *O* represents the equivalence point.

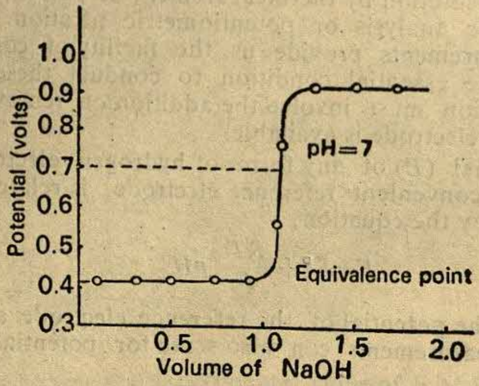


Fig. 16.11. Potentiometric titration curve of HCl vs NaOH.

The above principle is applied in displacement reactions involving neutralization. Many titrations involving precipitation and oxidation-reduction and sometimes reactions involving the decomposition and formation of soluble complexes are also studied potentiometrically.

The potentiometric method of titration offers a number of advantages in the determination of equivalence point;

(*i*) can be used in coloured or turbid solutions where ordinarily the use of coloured visual indicator would be useless.

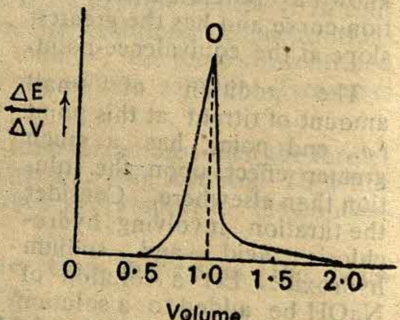


Fig. 16.12. Differential titration curve, HCl vs NaOH.

(*ii*) can be used where there is no satisfactory internal indicator to mark the equivalence point.

(*iii*) can be used where the change in potential (or pH) is rather too small at the end point to cause the complete change of coluor f he indicator.

TABLE 16.2

Official substances assayed by the potentiometeric method

Substance	*Titration Medium*	*Titrant*	*Indicator*
USP			
Caffine	Glacial acetic acid	0.05 N $HClO_4$	Glass
Chlorcyclizine HCl	,,	0.1N $HClO_4$	Glass
Chloroprocaine HCl	,,	0.1N $HClO_4$	Glass
Chloropromazine HCl	,,	0.1N $HClO_4$	Glass
Codeine phosphate	,,	0.1N $HClO_4$	Glass
Cyclizine HCl	,,	0.1N $HClO_4$	Glass
Hexachlorophene	Alcohol	0.1N NaOH	Glass
Homatropine HBr opthalmic solution	Chloroform	0.02N $HClO_4$	Glass
Phenobarbital	Alcohol	0.1N NaOH	Glass
Physostigmine	Acetic acid	0.02N $HClO_4$	Glass
Prochlorperazine Maleate	$CHCl_3$ – acetic acid	0.05N $HClO_4$	Glass
Sodium carboxymethyl cellulose	Glacial acetic acid	0.1N $HClO_4$	Glass
Sodium citrate	Glacial acetic acid	0.1N $HClO_4$	Glass
Anticoagulant sodium citrate solution	Glacial acetic acid	0.1N $HClO_4$	Glass
Aminobenzoic acid Tabs.	H_2O	0.1N $NaNO_2$	Platinum
Antazoline PO_4	Acetic acid	0.1N $HClO_4$	Glass
Bithionol	Acetone	0.1N NaOH	Glass
Calcium ammonium salicylate Tabs	H_2O	0.1N $NaNO_2$	Platinum
Calcium cyclamate	H_2O	0.1N $NaNO_2$	Platinum
Pipradol HCl	Glacial acetic acid	0.05N $HClO_4$	Glass
Propoxycaine HCl	H_2O	0.1N $NaNO_2$	Platinum
Trisodium phosphate	H_2O	0.1N NaOH	Glass
Sodium sulphabromomethazine	H_2O	0.1N $NaNO_3$	Platinum
Sulphamerazine Tabs	H_2O	0.1N $NaNO_2$	Platinum
Tetrahydrozoline HCl	Glacial acetic acid	0.1N $HClO_4$	Glass
Thenyldiamine HCl	Glacial acetic acid	0.1N $HClO_4$	Glass
Thiabendazole	Glacial acetic acid	0.1N $HClO_4$	Glass

(*iv*) a magnetic valve may be fitted to a potentiometer so that when a certain potential or pH is reached, the supply of titrant from a burette may be shut off. This permits automatic titrations to be performed.

Applications of potentiometric titrations. A growing number of chemotherapeutic substances are assayed by potentiometric titrations, some common examples are caffine, phenobarbital, codeine phosphate, chloroprocaine hydrochloride, sodium citrate, sulphacetamide, suphadiazine, sulphamerazine, tetrahydroline etc. Table 16.2 gives the official compounds which may be assayed potentiometrically along with the electrode pair which may be used for the titration.

Some pharmaceutical compounds which are affected significantly by oxidation-reduction are assayed potentiometrically; they include fats, oils, ascorbic acid, vitamin K, vitamin of the B group and morphine.

16.12. FUEL CELLS

A cell in which the combustion of a fuel is the chemical reaction, that provides the electrical energy, is called Fuel Cell. We can define a fuel cell as a galvanic cell in which a conventional fuel is supplied to one electrode and an oxidant, usually oxygen or air, to the other. Both electrodes and electrolytes present should be unaffected by the reaction. Electrodes also must meet stringent requirements. They must be good conductors and good electron sources or sinks and must not be consumed or deteriorated by the electrolyte, heat or electrode reactions. Hydrogen and oxygen are the reactants which are used in most of the fuel cells. A typical fuel cell is shown in Fig. 16.13.

The anodes and cathodes are made of porous nickel immersed in potassium hydroxide solution. A catalyst is added to increase the rate of reaction. The gases hydrogen and oxygen pass round the anodes and cathodes under pressure. The reactions occurring in a fuel cell can be symbolised as under:

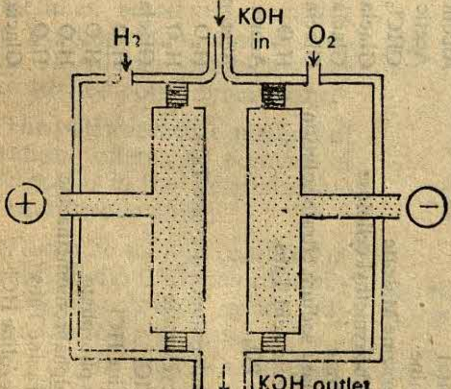


Fig. 16.13. Fuel Cell.

At the cathode:

$\frac{1}{2}O_2 + H_2O + 2e^- = 2OH^-$

At the anode:

$H_2 + 2OH^- = H_2O + 2e^-$

Overall reaction will be

$H_2 + \frac{1}{2}O_2 = H_2O$

It has been found that the production of electricity by means of a fuel cell is twice as efficient as the method, in which the fuel is burnt to power a steam turbine.

Fuel cells are being designed and fabricated for applications such as auxiliary power sources on spacecraft and submarines or other military vehicles to replace gasoline and diesel-powered generators and automobile engines, or to convert household sewage and other wastes to less noxious products. In future, fuel cells could be used to supply fresh water, heat and electricity to even the most remote villages.

16.13. POLAROGRAPHY

In an electrolysis-cell, having one polarizable electrode and other non-polarizable electrode, there occurs a phenomenon, which can be studied by means of current voltage curves. With the help of the current voltage-curve, the solution can be analysed. This method is known as *voltametry*. The technique in which the polarizable electrode consists of dropping mercury is known as *polarography*.

The dropping mercury electrode (DME). As the name suggests, the electrode is mercury in the form of a succession of droplets coming out from a glass capillary (internal diameter 0.03 to 0.05 mm). This has two advantages, first it provides the high hydrogen overvoltage and secondly, the electrode surface is being continually renewed and hence cannot become fouled. The diagrammatic representation of the apparatus is shown in Fig. 16.14.

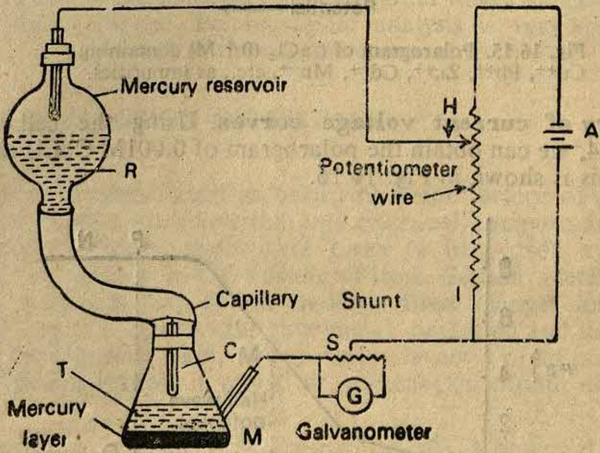


Fig. 16.14. Essential features of a polarograph.

The flask contains the experimental solution, which is saturated with an inert gas (nitrogen or hydrogen) by passing the gas through the tube *T*, *C* is a capillary from which the mercury falls at the rate of 20 to 30 drops per minute. The mercury level *M* serves as anode. The applied voltage is varied by means of a sliding contact along a potentiometer wire *I*. The galvanometer *G* is provided with a shunt *S* to measure the current strength. The complete current-voltage curve is thus obtained. The curve is obtained by automatic registering apparatus, known as *polarograph* and the curve so obtained is known as *polarogram*. The polarographic analysis of a solution of 0.1 M$CaCl_2$ containing Cu^{+2}, Pb^{+2}, Zn^{+2}, Cd^{2+}, Mn^{2+} etc. as impurities is shown in Fig. 16.15. The different species occupy their characteristic positions with respect to voltage in the polarogram, as shown below:

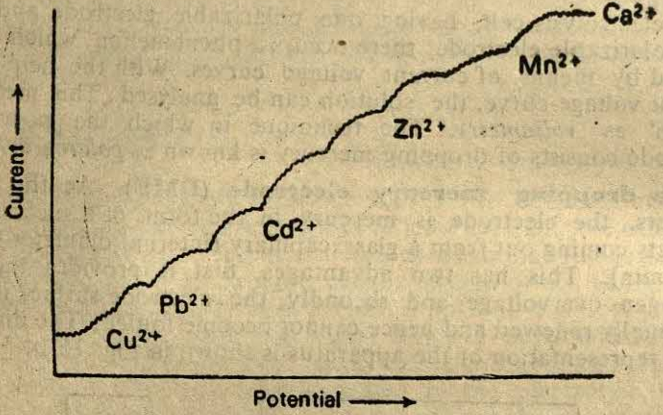


Fig. 16.15. Polarogram of $CaCl_2$ (0.1 M) containing Cu^{++}, Pb^{++}, Zn^{++}, Cd^{++}, Mn^{++}, etc., as impurities.

Theory of current voltage curves. Using the cell shown in Fig. 16.14, we can obtain the polarogram of 0.001M $CdCl_2$ in 0.01 M KCl. This is shown in Fig. 16.16.

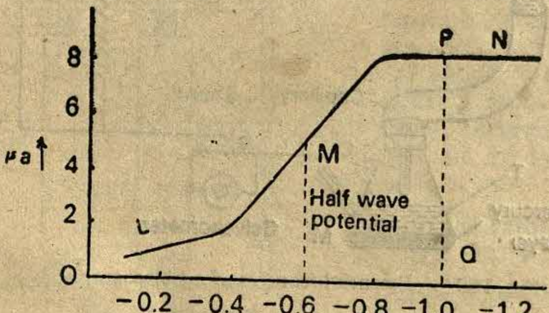


Fig. 16.16. Polarogram of $CdCl_2$ (0.001 M) in KCl.

The above curve can be divided into three regions *i.e.* *L*, *M* and *N*. At low potential (region) *L*, the current is very small due to the reduction of traces of impurities; this is known as *residual current*. On increasing the negative potential, the reduction of Cd^{++} ion starts, resulting in a sharp increase of current. When Cd^{++} ion is reduced completely, the current becomes almost constant (region *N*). This saturation is due to the local depletion of Cd^{++} ions in the vicinity of the *DME*. At this stage, the value of limiting current *i.e.*, *PQ*, is known as the diffusion-current and depends upon the concentration of the reducible species.

If n be the number of electrons involved in the cathodic reduction process; C the concentration of reducible substance in millimoles per litre, D the co-efficient of diffusion of the reducible substance in $cm^2/sec.$, m the mass of mercury flowing through the capillary in mg/sec. and t be the time between successive drops in seconds, the diffusion current i_d can be expressed using the relation

$$i_d = 607 n C D^{\frac{1}{2}} m^{\frac{2}{3}} t^{\frac{1}{6}} \qquad \ldots (16.26)$$

This is known as *Ilkovic equation* and can be used to estimate n or D under the conditions of the experiment. In practical polarography, stationary micro-electrodes are seldom used as it decreases the diffusion current and these have been replaced by rotating platinum electrode.

There are numerous uses to which polarography can be put to both in qualitative and quantitative analysis. Substances can be identified by knowing their characteristic half wave potentials ($E_{1/2}$) *i.e.*, the potential at the point on the polarogram where the current is half the diffusion current. Polarographic analysis is very useful in determining the structures of the organic compounds.

16.14. THE CORROSION OF METALS

Corrosion is a chemical reaction occurring at the surface of metals by which the metals are converted into chemical compounds. For example, iron, in moist atmosphere turns to iron oxide and the phenomenon is known as the rusting of iron. Certain metals like gold, silver, platinum, etc. do not undergo these changes and are called 'noble' metals. Due to the slow metal oxidation and the formation of impermeable skin, the corrosion is not a rapid process, though the process is rapid in moist air, presence of sulphur dioxide and water.

As the corrosion is an electro-chemical process, a potential difference is set up between the points of the surface, resulting in the formation of chemical-cell of the type system shown in Fig. 16.9. If we have copper and iron junction dipped into a salt solution, copper, being more electropositive, will act as the positive pole or anode whereas iron will behave like cathode. This will result in a flow of electrons from iron to copper. Inside the solution, iron is anode and copper is cathode as shown in Fig. 16.17.

Due to the anode reaction iron will be dissolved as ferrous ions, but at the cathode, Na^+ or H^+ ions will be discharged. Also due to alternative reaction, soluble oxygen will be converted to OH^- ions, as given below:

$$O_2+H_2O+4e^- \longrightarrow 4OH^- \quad \ldots (16.27)$$

These OH^- ions are attracted by the anode where they combine with Fe^{++} ions to form ferrous hydroxide. Thus iron near the junction is corroded whereas there is no effect on the copper.

A similar situation arises with single metals. For example, if there is a break on the oxide film on the iron surface, the oxide layer behaves as cathode whereas the exposed iron becomes anode. This facilitates the corrosion.

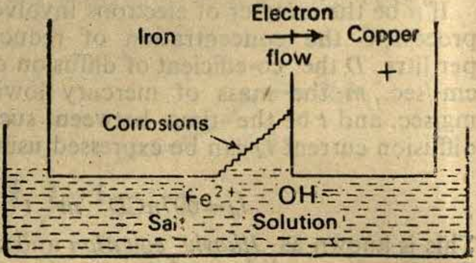


Fig. 16.17. Electrolytic corrosion at the junction between two metals (Fe—Cu).

This process can be resisted by a number of methods such as:

(1) by alloying the metal with suitable materials *i.e.*, stainless steel (Cr and Ni alloy).

(2) by applying a protective coating of paint or of a less corrodiable metals *i.e.*, Ag, Au, Cu, etc.

(3) by the protection of the cathode.

PROBLEMS

1. Devise cells in which cell reactions are the following:

(*a*) $H_2+I_2 \rightleftharpoons 2\,HI$

(*b*) $S_2O_8^{2-}+2I^- \rightleftharpoons I_2+2SO_4^{2-}$

(*c*) $2Fe^{2+}+CH_3CHO+H_2O \rightleftharpoons 2Fe^{2+}+CH_3COOH+2H^+$

Write down the cells with proper regard for the sign convention.

Ans. (*a*) $Pt(H_2)/H^+; I^-/I_2\,(Pt)$;
(*b*) $Pt(I_2)/I^-/ : SO_4^{2-}, S_2O_8^{2-}/Pt$;
(*c*) $Pt/CH_3CHO, CH_3\,COOH/Fe^{2+}\ Fe^{3+}/Pt$.

2. (*a*) The two electrodes in a galvanic cell are called the anode and the cathode. Reduction occurs at the cathode and oxidation at the anode. In Cu—Zn cell, which electrode is the anode and which is the cathode.

Ans. Cu electrode is cathode;
Zn electrode is anode.

(*b*) The oxidation-reduction reactions in an electron transfer reaction are called half cell reactions. Write down the half cell reaction for the reduction of H_2O in the reaction between Na and H_2O.

Ans. $H_2O+e^- \rightarrow \frac{1}{2}H_2+OH^-$

3. What is a reversible electrode? What type of reversible electrodes are commonly known? Explain with examples?

4. What do you understand by single electrode potential? How can it be measured experimentally?

5. When a silver-silver chloride and a calomel electrode are incorporated in the same cell, the reaction that takes place as the cell supplies current is:

$$Ag(s)+\tfrac{1}{2}Hg_2Cl_2(s)=Hg(l)+AgCl(s)$$

The EMF of the cell is 0.0455V at 298K and the temperature coefficient $\left(\frac{\partial E}{\partial T}\right)_p$ is $0.000338VK^{-1}$. Calculate $\triangle G$, $\triangle S$ and $\triangle H$ for the reaction. What would be the values for the reaction:

$$2Ag(s)+Hg_2Cl_2(s)=2Hg(l)+2AgCl(s)$$

[**Ans.** $\triangle G=-4390J$; $\triangle S=32.6JK^{-1}$; $\triangle H=5330J$; for the doubled reaction all these values will be doubled].

6. Calculate the EMF at 25°C of the cell:

$$Pt, H_2 \left|\begin{matrix}0.2 \text{ mol dm}^{-3}\\ \text{formic acid}\end{matrix}\right\|\begin{matrix}0.5 \text{ mol dm}^{-3}\\ \text{acetic acid}\end{matrix}\left| H_2, Pt\right.$$

given that the dissociation constant of formic acid and acetic acid are 1.77×10^{-4} and 1.75×10^{-5} respectively at 25°C. Assume that the liquid junction potential has been eliminated and that activity coefficients are unity.

[**Ans.** —0.018V]

7. Calculate the E.M.F. for the cell

$$Zn/Zn^{+2}(1M) \parallel Ag^{+}(1M)/Ag$$

Given $E^{\circ}_{Zn-Zn^{2+}}=+0.762$ volts (oxidation potential)

$E^{\circ}_{Ag^{+}-Ag}=0.800$ volts (reduction potential)

Ans. +1.562 volts

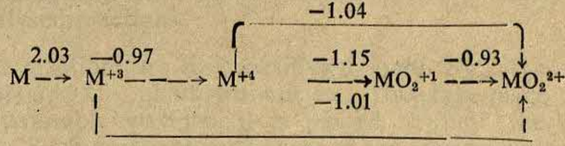
(*b*) For the reaction taking place in the cell

$$Zn/Zn^{+2}(aq) \parallel Cu^{+2}(aq)/Cu$$

the standard free energy change at 25°C is -50.79 kcal mol^{-1}. Calculate the E.M.F. at 25°C if the concentrations of zinc ions and copper ions are 0.015 mole $litre^{-1}$ and 0.0370 mole $litre^{-1}$ respectively.

Ans. 1.111 volts

8. Given below is a potential diagram indicating the standard oxidation potentials in volts for half reactions between the oxidation states of a hypothetical metallic element M.



where $M^{+3}+2H_2O\longrightarrow MO_2^{+2}+4H^{+1}+3e$ $E^{\circ}=-1.01$ volts

$M^{+1}+2H_2O\longrightarrow MO_2^{+1}+4H^{+1}+e$ $E^{\circ}=-1.15$ volts

Under standard conditions, (*a*) Will M react with Ag^{+}? (*b*) Will M^{+3} be reduced by Fe? (*c*) Will M^{+3} be oxidised by Cl_2? (*d*) Will M^{+4} be reduced by Sn? (*e*) Will M^{+4} and MO_2^{+} react ? (*f*) Will MO_2^{+} go to a higher and lower oxidation state simultaneously (disproportionate)?

9. Given the concentration cell.

$$Hg/Hg_2Cl_2(s)/HCl\ (0.01\ m) \parallel HCl\ (0.1\ m)/Hg_2Cl_2(s)\ Hg$$

where the sign $\parallel$ denotes a membrane through which only H^{+} ions can pass.

(*a*) Write the electrode reactions, the changes due to transference and the net cell reaction.

(*b*) Calculate the E.M.F. of the cell at 25°C.

Ans. (*a*) Anode reaction: $Hg+2Cl^-$ (0 01m)$=Hg_2Cl_2+2e^-$
Cathode reaction: $Hg_2Cl_2+2e^-=2Cl^-$ (0 1 m)$+2Hg$
Transference process: $2H^+$ (0 01 m)$=H^+$(0.1)
Net cell reaction: $2H^+$ (0.01 m)$+2Cl^-$ (0.01 m)
$=2H^+$ (0.1 m)$+2Cl^-$ (0.1 m)

(*b*) —0.118V

10. Explain the use of the calomel reference electrode for the determination of single electrode potentials. What is the function of a salt bridge used?

11. What are concentration cells? Derive an expression for the E.M.F. of a concentration cell. Calculate the potential developed on a copper electrode at 25° when it is dipping in a 0.1 m solution of copper sulphate. The standard electrode potential of $Cu/CuSO_4$ system is —0.337 volt at 25°.

Ans. −0.317 volt

12. Describe a quinhydrone electrode. Derive an expression for the potential of quinhydrone electrode. Explain how pH of a solution can be determined using this electrode. What are the limitations of a quinhydrone electrode?

13. Write notes on the following:

(*a*) Corrosion of metals

(*b*) Polarography

(*c*) Potentiometric titrations

(*d*) Glass electrode.

reactions which take place very slowly at ordinary temperature, but when the temperature is raised, they occur rapidly. It has been approximately found that for every 10°C rise in temperature, the velocity of the reaction gets doubled.

Effect of concentrations (or pressures). With the exception of zero order reactions, the rate of every chemical reaction is directly proportional to the concentrations (or pressures) of the reacting substances. Since concentrations of the reacting species do not remain constant during the course of the reaction and are continuously consumed during the course of the reaction, therefore, concentrations of the reactants decrease with the time. The variation of concentration (or the rate of reaction) with time is shown in Fig. 17.1. The rate is highest in the beginning, decreases gradually and becomes slower and slower with increase of time. Theoretically a reaction is never complete but for all practical purposes, it is assumed that the reaction becomes so slow after some time that it may be taken to be complete. Reverse is the case with the concentrations of the products. This can easily be understood from the curve in the diagram, which shows the variation of concentration of products, with time.

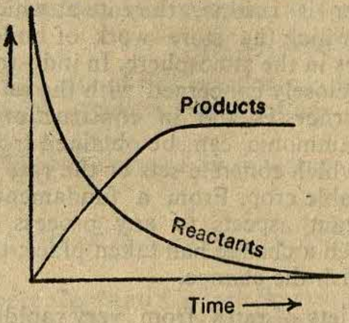


Fig. 17.1. Concentration versus time plot for reactants and products of a reaction.

Effect of a catalyst. The presence of a catalyst can increase or decrease the speed of a particular reaction *e.g.*, H_2 and O_2 do not combine. But in the presence of a small quantity of platinum which acts as a catalyst they combine and the reaction occurs rapidly. Similarly, a small amount of glycerine or acetanilide slows down the decomposition of hydrogen peroxide. The reactions which occur in the presence of a catalyst are known as catalysed reactions.

Some reactions are very sensitive to light *e.g.*, the reaction between H_2 and Cl_2, photosynthesis etc. They take place rapidly when light of suitable wavelength is passed through the reacting substances. Such reactions are known as the photochemical reactions.

Kinetically, reactions can be distinguished into two types, *i.e.*, (1) Homogeneous Reactions and (2) Heterogeneous Reactions. A homogeneous reaction takes place entirely in one phase, it may either be gas or solution. But, a heterogeneous reaction takes place in two or more phases, *e.g.*, gaseous reactions taking place on the surface of a solid catalyst or in the interior wall of the container.

Chapter 17

CHEMICAL KINETICS

17.1. INTRODUCTION

The rates at which chemical reactions occur are just as important to you as they are to the industrialist and the chemical engineers. At home you might be interested in the rate at which you can bake a cake or boil an egg. Out of doors, you might be interested in the rate at which your cycle or scooter is rusting, the rate at which *lettuces* are growing and the rate at which the store work of building is being weathered by acidic gases in the atmosphere. In industry, engineers and other workers will be closely concerned with the rates of chemical reactions in industrial processes and in constructional engineering, *i.e.* the rate at which ammonia can be obtained from nitrogen and hydrogen, the rate at which concrete sets or the rate of growth of a particular fruit or vegetable crop. From a fundamental point of view, there are two important aspects to any process of change. The first is the extent to which a change had taken place; the second is the time taken to accomplish the change.

Chemical reactions occur at a variety of rates from very rapid to very slow. For example, the paper on which this book is printed reacts extremely slowly with the atmospheric oxygen, whereas explosion is an extremely fast reaction. Chemical kinetics deals with the study of the speed or rate of chemical reactions and with the elucidation of their mechanism.

It has been observed that there are some reactions which proceed very rapidly and appear to be instantaneous *e.g.*, $N_2O_4 \rightarrow 2NO_2$, explosions and various ionic reactions. On the other hand, there are a number of reactions which proceed very slowly and require months and sometimes even years for completion at ordinary temperature *e.g.*, combination of Hydrogen and Oxygen to give water in the absence of a catalyst. Between these two extremes, there are many reactions, involving both organic and inorganic substances, whose velocities at room temperature can be easily measured.

Experimentally it has been found that the rate of a chemical reaction depends on the nature of the reacting species, the temperature, the concentrations (or pressures) of the reacting species and the presence of a catalyst.

Effect of temperature. Increase of temperature leads to an increase in the velocity of the reaction. There are many gaseous

17.2. THE REACTION RATE

The rate of a chemical reaction or alternatively its speed or velocity is defined as the rate at which concentrations of reacting species change with time and is denoted by $\frac{dC}{dt}$, where C is the concentration of any reacting substance and t is the time. If the concentration of reacting substance decreases with increasing reaction time as in the case of reactants, the minus sign is put before $\frac{dC}{dt}$ *i e.*, $-\frac{dC}{dt}$ is used. But if the concentration increases with time, plus sign is put before $\frac{dC}{dt}$.

Consider, for example, the reaction

$$H_2+I_2 \rightarrow 2HI$$

The rate of this reaction can be expressed in terms of the rate of change of concentration of any of the species involved.

Thus the rate of disapperance of $H_2 = -\frac{d(C_{H_2})}{dt}$ ... (17.1)

and rate of disappearance of $I_2 = -\frac{d(C_{I_2})}{dt}$ ... (17 2)

where C_{H_2} and C_{I_2} are the concentrations of H_2 and I_2 at time t.

Similarly, the rate of formation of the product HI is given by

$$\frac{+d(C_{HI})}{dt} \qquad \text{... (17.3)}$$

where C_{HI} is the concentration of HI at any time t.

The rates expressed by equations (17.1), (17.2) and (17.3) are related to each other through the stoichiometry of the reaction.

Since one molecule of H_2 combines with one molecule of I_2 to give two molecule of HI, the rate of decrease of C_{H_2} and C_{I_2} must be same and should be half the rate of increase of C_{HI} so that we have

$$-\frac{d(C_{H_2})}{dt} = \frac{-d(C_{I_2})}{dt} = \frac{d(C_{HI})}{\frac{1}{2}dt}$$

Therefore, while writing the equation, it is necessary to specify the species taken since rate for different species may be different.

In general, the rate of any reaction is written in terms of concentration. This follows from Law of Mass Action according to which the rate of any chemical reaction at each instant is directly proportional to the concentration of reacting species with each concentration terms raised to a power equal to the number of molecules of each reacting species.

Thus, for the reaction given above, the rate at which H_2 and I_2 react is given by

$$\frac{-dC}{dt}=kC_{H_2}.\ C_{I_2}$$

where k is a constant.

17.3. ORDER AND MOLECULARITY OF A REACTION

The order of a reaction is defined as the sum of the powers of the concentration terms in the rate equation. Consider the rate of the reaction given by

$$\text{Rate}=kC_1^{n_1}\ C_2^{n_2}\ C_3^{n_3}\ldots$$

where n_1, n_2, n_3 are the powers of the concentrations C_1, C_2, C_3 of reactants 1, 2, 3. . . respectively and k is a constant.

The overall order (n) of the reaction is

$$n=n_1+n_2+n_3+\ldots$$

and n_1, n_2, n_3 . . . etc. are the orders of the individual reactants 1, 2, 3 . . . respectively.

In order to illustrate it, consider the following reactions:

$$X \rightarrow \text{Product} \qquad \ldots (17.4)$$

$$X+Y \rightarrow \text{Products}$$

or

$$2X \rightarrow \text{Products} \qquad \ldots (17.5)$$

$$2X+Y \rightarrow \text{Products}$$

or

$$X+2Y \rightarrow \text{Products} \qquad \ldots (17.6)$$

The rate of reaction (17.4) is given by kC_X and the reaction is said to be of first order, the rate of reaction (17.5) is given by the kC_XC_Y or kC_X^2 and reaction is of second order and the rate of reaction (17.6) is given by $kC_X^2C_Y$ or $kC_XC_Y^2$ and the reaction is of third order.

It is not essential that the order of a reaction should be a whole number but can be *zero* or *fractional*. There are certain reactions, mostly heterogeneous reactions, for which the rate is zero or fractional.

Consider the decomposition of any gas on the surface of a solid catalyst. For the reaction to take place, the gas is first adsorbed on the surface of the catalyst and then decomposes. If the gas is strongly adsorbed *i.e.*, the entire surface of the solid is covered by the gas so that the surface gets saturated with the gas, reaction will be of zero order. But if the gas is weakly adsorbed, the reaction will be of first order. In the intermediate cases, the reaction will be of fractional order.

The molecularity of a reaction is given by the number of atoms or molecules of all the species participating in the reaction as given by the stoichiometric equation.

In the examples given above, since one molecule is involved in the reaction (17.4), it is unimolecular. Similarly, the reaction (17.5) is bimolecular as two molecules are involved and reaction (17.6) is termolecular as three molecules are involved.

For the reactions given above, it is seen that the order of reaction is same as the molecularity of a reaction. This identity between order and molecularity of a reaction does not hold in all cases.

Consider inversion of cane sugar. This can be written as

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}}+\underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6}+\underset{\text{Fructose}}{C_6H_{12}O_6}$$

Since two molecules of reactants are taking part in the reaction, hence it is bimolecular. However, this reaction is found to be of first order with respect to sugar. Thus the order of reaction is not the same as the molecularity and a distinction has to be made between the two. Order of a reaction is given by the number of atoms or molecules whose concentrations change during the reaction and determine the rate of the reaction. Thus, inversion of cane sugar is a first order reaction because rate is given by the concentration of sucrose only. Moreover, its concentration changes during the course of the reaction. Since water is present in excess, its concentration remains unaffected and hence does not contribute to the order of a reaction. But in determining molecularity of a reaction, all the molecules involved in the reaction are taken into consideration. Thus, inversion of cane sugar is an example of a bimolecular reaction with first order.

17.4. FIRST ORDER REACTIONS

Consider a first order reaction represented by

$$A \rightarrow \text{Products}$$

The rate of this reaction is directly proportional to the concentration of A. If C is the concentration of the reactant A at any time t, the rate of disappearance of A can be expressed mathematically as

$$\frac{-dC}{dt}=k_1C \qquad \ldots (17.7)$$

where k_1 is proportionality constant called the specific reaction rate or specific velocity constant for the first order rate equation. It can easily be seen from equation (17.7) that on putting $C=1$, k_1 becomes equal to the reaction rate. The specific rate constant for a first order reaction is a constant characteristic of the reaction and varies with temperature, but is independent of concentration. Since $\frac{dC}{dt}$ and C have the units of concentration/time and concentration respectively, therefore, k_1 has the units of reciprocal time, *i.e.*, t^{-1} as $k_1=-\left(\frac{1}{C}\right)\left(\frac{dC}{dt}\right)$. If time is given in seconds as is generally the case, the units of k_1 are sec^{-1}.

Equation (17.7) can also be written in another alternate but equivalent form. Let a mols/litre be the initial concentration of A. After time t, let x mols per litre of A have decomposed into the products. Therefore, remaining concentration of A at time $t=(a-x)$ mols/litre.

Putting $(a-x)$ for C into equation (17.7),

$$\frac{-d(a-x)}{dt}=k_1(a-x) \qquad \ldots (17.8)$$

But
$$\frac{-d(a-x)}{dt}=-\frac{da}{dt}-\left(-\frac{dx}{dt}\right)=\frac{dx}{dt}$$
$$\left(\frac{da}{dt}=0 \text{ because } a \text{ is a constant}\right)$$

Therefore, equation (17.8) becomes

$$\frac{dx}{dt}=k_1(a-x) \qquad \ldots (17.9)$$

This equation gives the rate of first order reaction in terms of initial concentration of the reactant and concentration of the reactant decomposed. Separating the variables and integrating this equation between the limits $x=0$ at $t=0$ and $x=x$ at time t;

$$\int_{x=0}^{x=x}\frac{dx}{(a-x)}=\int_{t=0}^{t=t}k_1 dt$$

$$[-ln(a-x]_{x=0}^{x=x}=k_1[t]_{t=0}^{t=t}$$

$$[-ln(a-x)+ln a]=k_1 t$$

and finally,
$$ln\,\frac{a}{a-x}=k_1 t \qquad \ldots (17.10)$$

Equation (17.10) is known as the kinetic equation for a reaction of the first order. This equation can also be written in the following alternate forms:

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x} \qquad \ldots (17.11)$$

and

$$t = \frac{2.303}{k_1} \log \frac{a}{a-x} \qquad \ldots (17.12)$$

Test for a first order reaction. A reaction is considered to be of first order if it strictly obeys equation (17.10). This can be verified by any of the following three methods:

(*i*) **Integration method**. In this method, the values of k_1 are calculated from equation (17.11) from a knowledge of initial concentration a and the concentrations of reacting substances at various time intervals. The value of a will be constant but that of $(a-x)$ will be different at different times. If the reaction obeys a first order equation, the various values of k_1 calculated will be the same. If k_1 values differ, higher order equations are tried until the assumed rate equation under consideration satisfactorily reproduce the observed data.

If equation (17.9) is integrated between the limits $x=x_1$ at $t=t_1$, and $x=x_2$ at $t=t_2$, we get the result

$$ln \frac{a-x_1}{a-x_2} = k_1(t_2-t_1)$$

This equation can also be used to calculate k_1 by taking any pair of concentrations of the reactants at any two time intervals.

(*ii*) **The graphic method**. Equation (17.10) can also be written in the form,

$$\log (a-x) = \left(\frac{-k_1}{2.303}\right) t + \log a$$

This equation is similar to an equation for a straight line. Hence a plot of log $(a-x)$ versus t for a first order reaction should be a straight line with a slope of $\left(\frac{-k_1}{2.303}\right)$ and intercept on the y-axis equal to log a as shown in Fig. 17.2. The rate constant k_1 can thus be calculated from the slope

$$k_1 = -2.303 \text{ (slope)}.$$

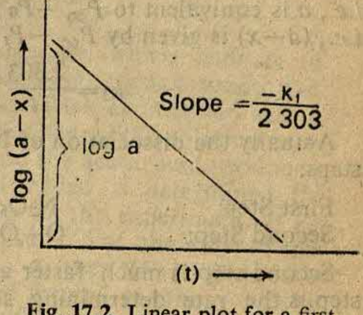


Fig. 17.2. Linear plot for a first order reaction.

(*iii*) **Fractional life method.** In this method, the time required to complete a definite fraction of the reaction is calculated, and is shown to be independent of concentration. The fraction generally taken is one-half of a given reactant. If $t_{1/2}$ is the time required to reduce the concentration of the reacting substance to half its initial value *i.e.*, for $x=\frac{a}{2}$, equation (17.10) becomes

$$t_{1/2}=\frac{2.303}{k_1}\log\frac{a}{a-\frac{a}{2}}=\frac{2.303}{k}\log 2.$$

$t_{1/2}$ is referred to as the half life period.

Thus, for any first order reaction, $t_{1/2}$ is a constant and independent of the initial concentration of the reactant. Consequently, in a first order reaction, the time required to reduce the amount of reactant from 1 mol/litre to 0.5 mol/litre will be the same as is required to reduce it from 10 mols/litre to 5 mols/litre in the same volume.

Similarly it can also be shown that the time required to complete $\frac{3}{4}$th or any other fraction of the reactant is also independent of initial concentration.

Examples of First Order Reactions

(*a*) **The decomposition of nitrogen pentoxide**. This can be studied both in gas and in solution. The stoichiometric equation for the gaseous decomposition of N_2O_5 is represented by

$$2N_2O_5(g)=4NO_2(g)+O_2(g)$$

Though this is a bimolecular reaction but is of first order and the rate law is given by

$$\frac{-dC_{N_2O_5}}{dt}-k_1\,C_{N_2O}$$

The course of this reaction is studied by determining the pressures of N_2O_5 at various intervals of time. Let P_0 is the initial pressure of N_2O_5 ($t=0$), P_t is the pressure after time t and P_∞ is the pressure when the reaction is complete. The initial concentration of N_2O_5, *i.e.*, a is equivalent to $P_\infty-P_0$ and concentration of N_2O_5 at time t, *i.e.*, $(a-x)$ is given by $P_\infty-P_t$

$$k_1=\frac{2.303}{t}\log\frac{P_\infty-P_0}{P_\infty-P_t}$$

Actually the dissociation of N_2O_5 takes place in the following two steps:

First Step: $N_2O_5 \rightarrow 2NO_2+O$
Second Step: $O+O \rightarrow O_2$

Second step is much faster as compared to first step. Hence first step is the rate determining step. In principle, it can be said that *if a reaction takes place in various steps, the rate of the reaction is determined by the slowest step.*

The decomposition of N_2O_5 is also studied in solution, generally carbon tetrachloride. Both N_2O_5 and NO_2 are soluble in CCl_4 and remain in solution while the oxygen evolved is insoluble and its volume is measured by using a suitable device. When the reaction is over, no more oxygen is evolved. Let V_∞ be the total volume of oxygen evolved at completion. This total volume will be proportional to the initial number of mols of N_2O_5 say a. Thus V_∞ is proportional to a. Similarly, the volume V_t of oxygen measured at any time t is proportional to the number of mols of oxygen formed and hence is proportional to x in equation (17.10). Thus the concentration of N_2O_5, $(a-x)$, left at time t, is proportional to $(V_\infty - V_t)$. Thus substituting V_∞ for a and $(V_\infty - V_t)$ for $(a-x)$ in equation (17.10),

$$k_1 = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

(*b*) **Hydrolysis of methyl acetate in aqueous solution.** Since this reaction is very slow, therefore, it is studied in the presence of a small amount of mineral acid which acts as a catalyst. The reaction is represented by

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

The rate of this reaction is given by

$$\frac{dx}{dt} = K.\, C_{CH_3COOCH_3} .\, C_{H_2O}$$

But, since water is present in large excess, its concentration is almost constant and, therefore, rate equation reduces to

$$\frac{dx}{dt} = K' .\, C_{CH_3COOCH_3}$$

i.e.. the rate of the reaction is determined only by the concentration of the methyl acetate and hence this reaction is of the first order and obeys first order equation.

Reactions of this type are known as *Pseudo Unimolecular Reactions.*

This reaction is studied as follows:

A definite amount of the reacting solution, which consists of methyl acetate dissolved in water, containing a small quantity of HCl, is removed with pipette, into a conical flask and titrated with a standard solution of alkali. The volume of the alkali solution used is equivalent to the total of HCl added and the acetic acid produced due to hydrolysis. This amount of HCl added is determined by titrating the reaction mixture at the start of the experiment. If V_0 is the volume of alkali used to neutralise HCl at the start of the reaction and V_t the volume after time t, then $(V_t - V_0)$ is the volume required to neutralise acetic acid formed at time t. This is identified with x in the rate equation for first order reaction. When the reaction is complete, let V_∞ be the volume of alkali required for neutralization of the reaction mixture. (This now consists of HCl and acetic acid formed by complete hydrolysis of ester.) Thus, the initial concentration of methyl acetate, *i.e.*, a is proportional to $(V_\infty - V_0)$ and the concentration of methyl acetate at any time t, *i.e.*, $(a-x)$ is proportional to $(V_\infty - V_0)-(V_t - V_0)=(V_\infty - V_t)$.

Therefore, equation for the first order reaction is written as

$$k_1 = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}.$$

(*c*) **Inversion or hydrolysis of cane sugar**. This is another example of pseudo unimolecular reaction similar to the hydrolysis of ester and is represented as

$$\underset{\text{Surcrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\substack{\text{Glucose}\\\text{Dextro}}}{C_6H_{12}O_6} + \underset{\substack{\text{Fructose}\\\text{Laevo}}}{C_6H_{12}O_6}$$

This reaction is studied by measuring the angles of rotation of reaction mixture at various times. Let α_0 ann α_∞ be the angles of rotation at the start ($t=0$) and when the reaction is complete respectively and α_t is the angle at any time t. Then $(\alpha_0 - \alpha_\infty)$ is proportional to the initial amount of sucrose, *i.e.*, a and $(\alpha_t - \alpha_0)$ is proportional to the amount of sucrose left at time t, *i.e.*, $(a-x)$. Therefore, rate equation becomes

$$k_1 = \frac{2.303}{t} \log \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$$

(*d*) **Decomposition of benzene diazonium chloride $C_6H_5N=NCl$ in water**. This reaction takes place on heating and can be written as

$$C_6H_5N=NCl + H_2O \longrightarrow C_6H_5OH + HCl + N_2$$

The reaction is studied by measuring the volume of N_2 produced by decomposition of $C_6H_5N=NCl$ at various time intervals. The volume of N_2 evolved is proportional to the decrease in concentration of diazonium salt. If V_∞ is the volume of N_2 measured at the end of the reaction and V_t, the volume at any time t then

$a \propto V_\infty$ and $(a-x) \propto (V_\infty - V_t)$

Therefore,

$$k_1 = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

Problem 17.1. From the following data, show that the decomposition of hydrogen peroxide in aqueous solution is a first order reaction.

Time in minutes	0	5	10	20
$KMnO_4$ (ml)	46.1	37.1	29.8	19.6

Solution. For a first order reaction,

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$$

Here $a=46.1$, the volume of $KMnO_4$ used at zero time and $(a-x)$ corresponds to the volume of $KMnO_4$ used at any time.

Substituting the various values in the above equation, we get

$$t=5 \qquad k_1=\frac{2.303}{5}\log\frac{46.1}{37.1}=0.0435$$

$$t=10 \qquad k_1=\frac{2.303}{10}\log\frac{46.1}{29.8}=0.0438$$

$$t=20 \qquad k_1=\frac{2.303}{20}\log\frac{46.1}{19.6}=0.0429$$

The constancy of k_1 shows that the reaction under consideration is of first order.

Problem 17.2. The following data was obtained on the hydrolysis of methyl acetate at 25°C in the presence of 0.35N hydrochloric acid which was used as a catalyst.

Time (seconds)	0	1200	4500	7140	∞
ml. of alkali used	24.36	25.85	29.32	31.72	47.15

From the above data, show that the hydrolysis of methyl acetate is a first order reaction.

Solution. Since for a first order reaction,

$$k_1=\frac{2.303}{t}\log\frac{V_\infty-V_0}{V_\infty-V_t}$$

where the terms V_0, V_t and V_∞ are the volume of alkali used at the start of the reaction, after time t and at the end of the reaction respectively.

The value of k_1 calculated at different times is given below:

$$t=1200 \qquad k_1=\frac{2.303}{1200}\log\frac{47.15-24.36}{47.16-25.86}=5.62\times10^{-5}$$

$$t=1500 \qquad k_1=\frac{2.303}{4500}\log\frac{47.15-24.36}{47.15-29.32}=5.46\times10^{-5}$$

$$t=7140 \qquad k_1=\frac{2.303}{7140}\log\frac{47.15-24.36}{47.15-31.72}=5.44\times10^{-5}$$

Since k_1 is constant, hence hydrolysis of methyl acetate is a first order **reaction.**

Problem 17.3. The optical rotations of sucrose in 0.5 N HCl at various time intervals are given below,

Time (minutes)	0	10	20	40	∞
Rotation (degrees)	+32.4	+28.8	+25.5	+19.6	−11.1

Show that the reaction is of first order.

Solution. For the reaction under consideration,

$$k_1=\frac{2.303}{t}\log\frac{\alpha_0-\alpha_\infty}{\alpha_t-\alpha_\infty}$$

where α_0, α_t and α_∞ represent the optical rotation at the start of the reaction, at time t and at the completion of the reaction.

Hence $\alpha_0-\alpha_\infty=+32.4-(-11.1)=+43.5$

t	$\alpha_t-\alpha_\infty$	$\frac{2.303}{t}\log\frac{\alpha_0-\alpha_\infty}{\alpha_t-\alpha_\infty}$
10	39.9	$\frac{2.303}{10}\log\frac{43.5}{39.9}=0.008625$

20	36.6	$\frac{2.303}{20} \log \frac{43.5}{36.6} = 0.008625$
40	30.7	$\frac{2.303}{40} \log \frac{43.5}{30.7} = 0.008117$

The constancy of k_1 clearly shows that the reaction is of first order.

Problem 17.4. Decomposition of benzene diazonium chloride was studied at a constant temperature by measuring the volume of N_2 evolved at various intervals of time. The following data was obtained:

Time (minutes)	0	20	50	70	∞
N_2 (ml)	0	10	25	33	162

From the above data, show that the reaction is of first order.

Solution. For the reaction under consideration,

$$k_1 = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

where V_∞ and V_t represent the volume of nitrogen measured at the end of the reaction and at time t respectively.

Substituting the various values in the above equation:

$$t=20 \qquad k_1 = \frac{2.303}{20} \log \frac{162}{162-10} = 0.00322$$

$$t=50 \qquad k_1 = \frac{2.303}{50} \log \frac{162}{162-25} = 0.00336$$

$$t=70 \qquad k_1 = \frac{2.303}{70} \log \frac{162}{162-35} = 0.00326$$

The constancy of k_1 clearly shows that the reaction is of first order.

17.5. SECOND ORDER REACTIONS

For a second order reaction, the rate depends on two variable concentration terms which may or may not be same.

Case I. When the two reacting molecules are different with different concentrations.

Consider a bimolecular reaction of the type

$$A + B \longrightarrow \text{Products}$$

If C_A and C_B are the concentrations of A and B respectively at any time t, then assuming that the reaction is of first order with respect to both A and B, the overall order is second and reaction rate is given by

$$\frac{-dC_A}{dt} = \frac{-dC_B}{dt} = k_2 C_A C_B \qquad \ldots (17.13)$$

where k_2 is the specific rate constant for a second order reaction and becomes the rate of the reaction when both C_A and C_B are unity. It depends on the nature of the reactants and varies with temperature. Its units are $\text{conc}^{-1}\ \text{time}^{-1}$.

To get equation (17.13) into an integral form, both C_A and C_B are expressed in terms of a single variable. Let a mols/litre and b mols/litre are the initial concentrations ($t=0$) of A and B respectively and x mol/litre is the amount of each that has reacted at time t. Therefore, at time t, $C_A=(a-x)$ and $C_B=(b-x)$ and equation (17.13) becomes

$$\frac{dx}{dt}=k_2(a-x)(b-x)$$

Separating the variables,

$$k_2dt=\frac{dx}{(a-x)(b-x)} \qquad \ldots (17.14)$$

Now $\frac{1}{(a-x)(b-x)}$ on the right of equation (17.14) is broken into partial fractions as shown below.

$$\frac{1}{(a-x)(b-x)}=\frac{A}{(a-x)}+\frac{B}{(b-x)}$$

or $$A(b-x)+B(a-x)=1$$

If $x=a$, then

$$A(b-a)=1 \text{ or } A=\frac{1}{b-a}$$

and when $x=b$, then

$$B(a-b)=1 \text{ or } B=\frac{1}{a-b}$$

Thus, $$\frac{1}{(a-x)(b-x)}=\frac{1}{(b-a)(a-x)}+\frac{1}{(a-b)(b-x)}$$

$$=\frac{1}{a-b}\left[\frac{1}{(b-x)}-\frac{1}{(a-x)}\right]$$

Therefore, equation (17.14) becomes

$$k_2dt=\frac{1}{(a-b)}\left[\frac{1}{(b-x)}-\frac{1}{(a-x)}\right]dx$$

Integrating this expression in the limits that $x=0$ at $t=0$ and $x=x$ at $t=t$

$$\int_{t=0}^{t=t} k_2dt=\frac{1}{(a-b)}\int_0^x\left[\frac{1}{(b-x)}-\frac{1}{(a-x)}\right]dx$$

$$k_2\Big[\,t\,\Big]_0^t=\frac{1}{a-b}\Big[-ln(b-x)+ln(a-x)\Big]_0^x$$

$$k_2t=\frac{1}{a-b}\Big[-ln(b-x)+ln(a-x)+lnb-lna\Big]$$

$$=\frac{1}{a-b}\,ln\,\frac{b(a-x)}{a(b-x)}$$

or
$$k_2=\frac{2.303}{t(a-b)}\log\frac{b(a-x)}{a(b-x)} \qquad \ldots (17.15)$$

Case II. When the concentrations of the reacting molecules are same *i e.*, $a=b$ or both the reacting molecules are same.

Under these conditions, the rate of the reaction at time t can be written as

$$\frac{dx}{dt}=k_2(a-x)^2$$

Separating the variables and integrating between the limits $x=0$ at $t=0$ and $x=x$ at $t=t$

$$\int_0^t k_2dt=\int_0^x\frac{dx}{(a-x)^2}$$

$$k_2\Big[\,t\,\Big]_0^t=\Big[\frac{1}{a-x}\Big]_0^x$$

$$k_2t=\frac{1}{a-x}-\frac{1}{a}$$

or
$$k_2=\frac{1}{t}\cdot\frac{x}{a(a-x)} \qquad \ldots (17.16)$$

Equations (17.15) and 17.16) are the expressions for second order reactions.

Tests for a Second Order Reaction

These are similar to those used for the first order reactions.

(*i*) **Integration method**. The values of the specific rate constant, k_2, are calculated by substituting the amounts of reacting substances consumed after various intervals of time and those of a and b or a in either equation (17.15) or (17.16) depending on the concentrations of the two reacting molecules. The various values of k_2 calculated for a series of time intervals will be same for a second order reaction.

(*ii*) **Graphical method.** Equation (17.15) can be written as:

$$\frac{2.303}{(a-b)}\log\frac{(a-x)}{(b-x)}=k_2t-\frac{2.303}{a-b}\log\frac{b}{a}$$

This is similar to an equation for a straight line. Therefore, for a second order reaction, the plot between $\frac{2.303}{(a-b)}\log\frac{(a-x)}{(b-x)}$ versus

t should be a straight line with a slope k_2 and intercept

$$\left(-\frac{2.303}{a-b}\log\frac{b}{a}\right)$$

as shown in Fig. 17.3.

Similarly for reactions having same concentrations, equation (17.16) is rewritten as

$$\frac{1}{a-x}=k_2t+\frac{1}{a}$$

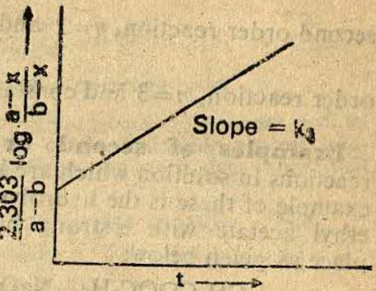


Fig. 17.3. Linear plot for a second order reaction.

A plot of $\frac{1}{(a-x)}$ versus t will be linear with a slope k_2 and intercept on the concentration axis will be $\frac{1}{a}$.

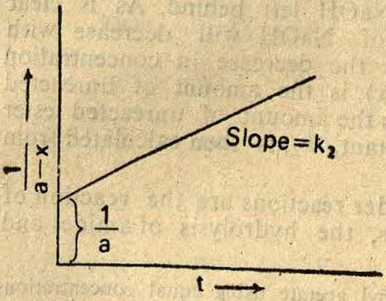


Fig. 17.4. Linear plot for a second order reaction.

(*iii*) **The fraction life method.** This is used only for those reactions where the concentrations of the two reacting molecules are same or the two reacting molecules are similar. Thus using equation (17.16), half life period, $t_{1/2}$ is given by setting $x=\frac{a}{2}$

$$t_{1/2}=\frac{1}{k_2}\frac{\left(\frac{a}{2}\right)}{a\left(\frac{a}{2}\right)}=\frac{1}{k_2a}.$$

This shows that half life period for a second order reaction varies inversely as the initial concentration.

In general half life period for any reaction of nth order varies inversely as $(n-1)$ power of the initial concentration *i.e.*, for the reaction,

$$nA \rightarrow \text{Products},$$

$$t_{1/2}\propto\frac{1}{a^{n-1}} \text{ or } t_{1/2}=\text{constant}\times\frac{1}{a^{n-1}}$$

The magnitude of the constant depends on the order of a reaction. For a first order reaction, $n=1$ and constant is $\frac{2.303}{k_1}\log 2$, for a second order reaction, $n=2$ and constant is $\frac{1}{k_2}$ and for a third order reaction, $n=3$ and constant is found to be $\frac{3}{2}k_3$.

Examples of second order reactions. There are many reactions in solution which are kinetically of second order. A typical example of these is the hydrolysis or saponification of an ester *e.g.*, ethyl acetate with a strong base *e.g.*, NaOH. The reaction takes place as given below:

$$CH_3COOC_2H_5+NaOH=CH_3COONa+C_2H_5OH$$

The reaction mixture is prepared by mixing a known amount of ethyl acetate with a known amount of NaOH. Let a and b be the initial concentrations of ethyl acetate and NaOH respectively. The course of the reaction is followed by removing a definite quantity of the reacting mixture from time to time and titrating with standard acid to know the concentration of NaOH left behind. As is clear from reaction, the concentration of NaOH will decrease with increase in the reaction time. If x is the decrease in concentration of NaOH at any time t, then $(b-x)$ is the amount of unreacted NaOH at time t. Similarly $(a-x)$ is the amount of unreacted ester at time t. The specific rate constant, k_2, is then calculated from equation (17.15).

The other examples of second order reactions are the reaction of alkyl halides with tertiary amines, the hydrolysis of amides and acetals, benzoin condensation etc.

Problem 17.5. In the hydrolysis of ethyl acetate using equal concentrations of ester and NaOH, the following results were obtained:

t(minutes)	0	5	15	25	35
HCl (ml)	16.0	10.24	6.13	4.32	3.41

Show that the reaction is of second order.

Solution. The equation for the second order reactions, using equivalent concentrations of the reactants is

$$k_2=\frac{1}{t}\times\frac{x}{a(a-x)}$$

In this case, $a \propto T_0$ (Volume of acid used at zero time)

$a-x \propto T_t$ (Volume of acid used at time t)

$x \propto T_0-T_t$

The value of k_2 is calculated as given below:

$a=16.0$

Time t	a-x	x	$k_2=\frac{1}{t}\times\frac{x}{a(a-x)}$
5	10.24	5.66	$\frac{1}{5}\times\frac{5.76}{16\times10.24}=0.00698$
15	6.13	9.87	$\frac{1}{15}\times\frac{9.87}{16\times6.13}=0.0067$

25	4.32	11.68	$\frac{1}{25}\times\frac{11.68}{16\times4.32}=0.0069$
35	3.41	12.59	$\frac{1}{35}\times\frac{12.59}{16\times3.41}=0.0066$

Since the value of k_2 is constant, the reaction is of second order.

Problem 17.6. The hydrolysis of ethyl nitrobenzoate by aqueous sodium hydroxide was followed, at 25°C, by titration of the hydroxide against standard acid at different stages in the reaction. From the given data, show that the reaction is of second order.

Time (seconds)	0	95	140	222	334	805	1364
ml of acid used	10	9.3	9.0	8.5	7.9	6.1	4.8

Solution. For the second order reaction

$$k_2=\frac{1}{t}\times\frac{x}{a(a-x)}$$

In the present case $a=10$

The value of k_2 is calculated as follows

Time	$a-x$	x	$k_2=\frac{1}{t}\times\frac{x}{a(a-x)}$
95	9.3	0.7	$\frac{1}{95}\times\frac{0.7}{10\times9.3}=7.92\times10^{-2}$
140	9.0	1.0	$\frac{1}{140}\times\frac{1.0}{10\times9.0}=7.93\times10^{-2}$
222	8.5	1.5	$\frac{1}{222}\times\frac{1.5}{10\times8.5}=7.94\times10^{-2}$
334	7.9	2.1	$\frac{1}{334}\times\frac{2.1}{10\times7.9}=7.95\times10^{-2}$
805	6.1	3.9	$\frac{1}{805}\times\frac{3.9}{10\times6.1}=8.05\times10^{-2}$
1364	4.8	5.2	$\frac{1}{1364}\times\frac{5.2}{10\times4.8}=7.93\times10^{-2}$

The constancy of k_2 shows that the reaction is of second order.

Problem 17.7. It has been determined experimentally that the sequence of steps for a chemical reaction are as follows:

$$A+B\rightarrow C \quad \text{(slow)}$$
$$C+B\rightarrow D \quad \text{(fast)}$$

What is the rate equation and overall chemical equation?

Solution. The overall chemical equation will be obtained by adding the above equations *i.e.*

$$\begin{array}{l} A+B\rightarrow C \quad \text{(slow)} \\ \underline{C+B\rightarrow D \quad \text{(fast)}} \\ A+2B\rightarrow D \end{array}$$

Since the rate of a reaction is controlled by the slow step, the rate equation will be

$$\text{rate}=k[A]\,[B].$$

17.6. REACTIONS OF THE THIRD ORDER

A termolecular reaction is said to be of third order when the rate depends on three variable concentration terms. Consider the most general form of a termolecular reaction in which three different molecules are reacting such as

$$A+B+C \rightarrow \text{Products.}$$

The rate of the reaction at each instant is given by

$$\frac{-dC_A}{dt}=\frac{-dC_B}{dt}=\frac{-dC_C}{dt}$$

$$=k_3 C_A C_B C_C \qquad \ldots (17.17)$$

If a, b and c are the initial concentrations A, B and C respectively and x is the decrease in concentration of each at any time t, then the rate equation reduces to

$$\frac{dx}{dt}=k_3(a-x)(b-x)(c-x) \qquad \ldots (17.18)$$

For the special case when $a=b=c$ or for a reaction in which all the three reacting molecules are same *i.e.*,

$$3A \rightarrow \text{Products,}$$

the rate equation becomes

$$\frac{dx}{dt}=k_3(a-x)^3 \qquad \ldots (17.19)$$

On separating the variables and integrating between the limits $x=0$ at $t=0$ and $x=x$ at any time t,

$$\int_0^t k_3 t=\int_0^x \frac{dx}{(a-x)^3}$$

$$k_3\Big[\, t\, \Big]_0^t=\Big[\frac{1}{2(a-x)^2}\Big]_0^t$$

or

$$k_3 t=\frac{1}{2(a-x)^2}-\frac{1}{2a^2}.$$

This can also be written as

$$k_3=\frac{1}{2t}\left[\frac{1}{(a-x)^2}-\frac{1}{a^2}\right] \qquad \ldots (17.20)$$

Equation (17.20) can be tested by the same methods as explained for first and second order reactions *i.e.*, integration method, the graphical method and fractional life method.

From equation (17.20), half life period is given by equation:

$$t_{1/2}=\frac{3}{2k_3 a^2}$$

which is in accordance with the general definition of half life period.

Examples of third order reaction. There are very few (only five) examples of third order reactions in the gaseous phase and each example involves two molecules of nitric oxide as one of the reactants and the other reactant is a molecule of either chlorine, bromine, oxygen, hydrogen or deuterium The general reaction is

$$2NO + X \rightarrow \text{Products}$$

where X can be either Cl_2, Br_2, O_2, H_2 or D_2.

The reaction with O_2, Br_2 and H_2 are as:

$$2NO + O_2 \rightarrow 2NO_2$$

$$2NO + Br_2 \rightarrow 2NOBr$$

$$2NO + H_2 \rightarrow N_2O + H_2O$$

The rate equation for these types of reactions is

$$\frac{dx}{dt} = k_3(a-2x)^2(c-x)$$

where a and c are the initial concentrations of NO and X respectively and x is the decrease in the concentration of each at any time t.

Integration of this equation in the limits when $t=0$, $x=0$ and when $t=t$, $x=x$, gives the following results:

$$k_3 = \frac{1}{t(2b-a)^2}\left[\frac{2x(2b-a)}{a(a-2x)} + ln\frac{b(a-2x)}{a(b-x)}\right]$$

Some examples of third order reaction in solutions are the interaction of stannous chloride and ferric chloride, oxidation of ferrous sulphate in water, the reaction between benzoyl chloride and alcohol in ether solution, reaction of triphenyl methyl (trityl) chloride with methanol in dry benzene etc.

Problem 17.8. The reduction of ferric chloride by stannous chloride was studied by Noyer. The reaction was followed by taking equivalent amounts (concentration = 0.0625) of the rectants in a flask kept in a thermostat, and withdrawing quantities from time to time, the time being noted. These were run into mercuric chloride to remove excess of stannous chloride and then the ferrous iron was determined by titrating against standard potassium dichromate solution. The results obtained are given below:

t (minutes)	1	3	7	40
x	0.01434	0.02664	0.03612	0.05058

Show that the reaction is of third order.

Solution. The reaction is written as

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$$

The third order rate expression when all the reactants are taken in equivalent amounts is given by

$$k_3 = \frac{1}{2t}\left(\frac{1}{(a-x)^2} - \frac{1}{a^2}\right)$$

For the reaction, $a = 0.06250$

The value of k_3 is calculated as given below:

t	x	$a-x$	$\frac{1}{2t}\left(\frac{1}{(a-x)^2}-\frac{1}{a^2}\right)$
1	0.01434	0.04816	$\frac{1}{2\times1}\left(\frac{1}{(0.04816)^2}-\frac{1}{(0.0625)^2}\right)=87$
3	0.02664	0.03586	$\frac{1}{2\times3}\left(\frac{1}{(0.03586)^2}-\frac{1}{(0.0625)^2}\right)=87$
7	0.03612	0.02638	$\frac{1}{2\times7}\left(\frac{1}{(0.02638)^2}-\frac{1}{(0.0625)^2}\right)=84$
40	0.05058	0·01192	$\frac{1}{2\times40}\left(\frac{1}{(0.01192)^2}-\frac{1}{(0.0625)^2}\right)=85$

A fairly constant value of k_3 shows that the reaction is of third order.

17.7. ZERO ORDER REACTIONS

"Zero order reactions are those reactions in which the concentrations of the reactants remain constant during the course of the reaction and, therefore, the rate is independent of the concentrations of such reacting molecules."

There are number of examples of zero order reactions. Some quite familiar examples are: reaction between $H_2(g)$ and $Cl_2(g)$ in the presence of sunlight; the decomposition of hydrogen iodide and ammonia at the surface of gold and molybdenum respectively, etc. (Au and Mo act as catalysts).

In order to understand zero order reactions, consider the decomposition of HI on the surface of gold. The reaction is

$$2HI(g) \rightarrow H_2(g)+I_2(g)$$

At very high pressures, the surface of gold, at which reaction occurs, will be fully covered by reacting molecules due to adsorption. At this stage, further increase of concentration of HI(g) will have no effect as there is no bare space available for absorption on the surface. Therefore, the rate of the reaction will become constant and the reaction will be of zero order.

Thus the rate of disappearance of HI(g) is written as

$$\frac{-dC_{HI}}{dt}=k_0 C^0{}_{HI}$$

where k_0 is the specific rate constant for zero order reaction.

Zero order reactions are also encountered when the concentration of reactant is so large that it practically remains constant during the course of the reaction.

If x is the amount of the product, then for a zero order reaction,

$$\frac{dx}{dt}=k_0$$

Integrating between the limits that when $t=0$, $x=0$ and at time t, $x=x$,

$$x+k_0t$$

i.e., for a zero order reaction, concentration of product increases with increase of reaction time.

17.8. EFFECT OF TEMPERATURE ON REACTION VELOCITY

The temperature has got a significant effect on the rate of the reaction. It has been observed experimentally that increase in temperature leads to a remarkable increase in the rate of a chemical reaction and hence in rate constants. Variation of rate or rate constant of a reaction with temperature belongs to any one of the five forms shown in Fig. 17.5.

Type I curve is obtained for most of the reactions. Type II curve is obtained for explosions. In this curve, a sudden rise in the rate of the reaction is shown. This happens at the ignition temperature. Type III of curve is obtained in catalytic hydrogenations and in enzyme reactions. Curve IV is obtained when carbon is oxidised. Curve V is obtained only for the reaction $2NO+O_2 \longrightarrow 2NO_2$. This is the only reaction which exhibits a negative temperature coefficient.

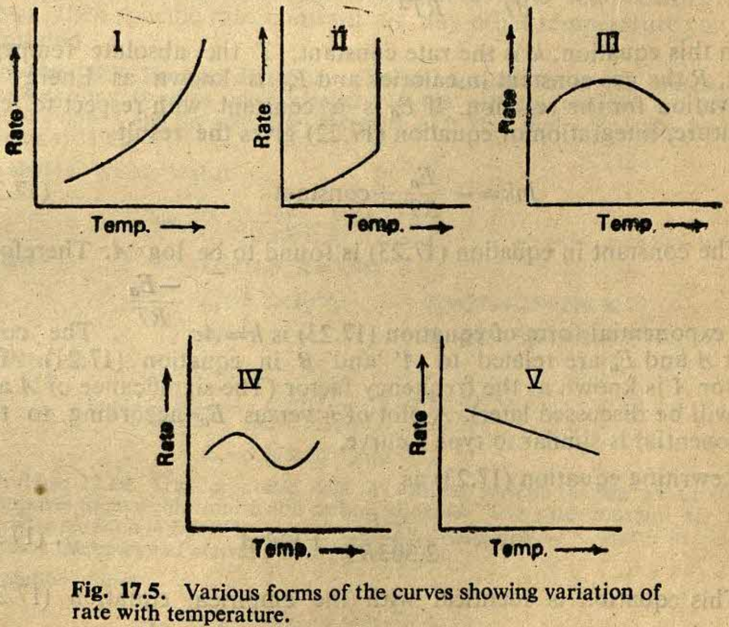


Fig. 17.5. Various forms of the curves showing variation of rate with temperature.

Type I corresponds to the curves as given by Arrhenius when he studied the variation of rate constant with temperature. Hence this is known as Arrhenius Temperature dependence while types II to V are referred to as anti-Arrhenius curves.

For homogeneous reactions, an important generalisation is that rate is doubled or trebled for every 10°C rise of temperature (Type I is in agreement with this statement). The first empirical equation to show the variation of rate constant (k) of a reaction with temperature (T) was suggested by Hood. His equation is

$$\log k = A' - \frac{B}{T} \qquad \ldots (17.21)$$

where A' and B are positive empirical constants and T is absolute temperature. The verification of this equation lies in the fact that a plot of $\log k$ versus $\frac{1}{T}$ is nearly a straight line with negative slope for most of the reactions.

This equation was theoretically justified by Van't Hoff in 1884. His arguments were based on the variation of equilibrium constants with temperature. Arrhenius extended his ideas and suggested a similar equation to show the variation of rate constant with temperature in the year 1889. The Arrhenius equation is,

$$\frac{d\ln k}{dT} = \frac{E_a}{RT^2} \qquad \ldots (17.22)$$

In this equation, k is the rate constant, T the absolute temperature, R the gas constant in calories and E_a is known as Energy of activation for the reaction. If E_a is a constant with respect to temperature, integration of equation (17.22) gives the result

$$\ln k = -\frac{E_a}{RT} + \text{constant} \qquad \ldots (17.23)$$

The constant in equation (17.23) is found to be log A. Therefore, the exponential form of equation (17.23) is $k = Ae^{\frac{-E_a}{RT}}$. The constant A and E_a are related to A' and B in equation (17.21). The factor A is known as the frequency factor (The significance of A and E_a will be discussed later). A plot of k versus E_a according to this exponential is similar to type I curve.

Rewriting equation (17.23) as

$$\log k = \frac{-E_a}{2.303RT} + \log A \qquad \ldots (17.24)$$

This equation is identical with the empirical equation (17.21). According to this equation, a plot of $\log k$ versus $\frac{1}{T}$ should be a straight line with a slope $\frac{-E_a}{2.303\,R}$ and intercept log A as shown in Fig. 17.6. Knowing the slope, the value of constant E_a which is characteristic of the reaction can be calculated *e.g.*, for the decomposition of N_2O_5, the slope is -5400. Hence E_a is given by

$$E_a=-(-5400)(2.303)(1.987)$$
$$=24{,}700 \text{ cals/mol.}$$

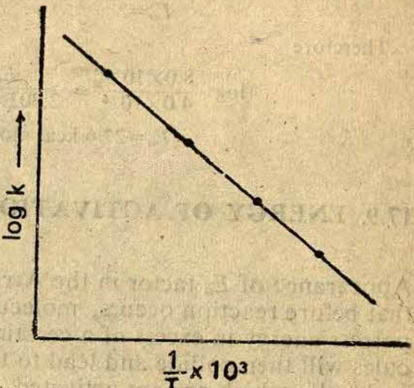


Fig. 17.6. Variation of log k with $1/T$ for the decomposition of N_2O_5.

E_a can also be determined if the specific rate constants are known at two different temperatures. If k_1 is the specific rate constant at temperature T_1 and k_2 at another temperature T_2, then from equation (17.24)

$$\log \frac{k_2}{k_1}=\frac{E_a}{2.303R}\left(\frac{T_2-T_1}{T_2T_1}\right) \qquad \ldots (17.25)$$

It is evident from this equation that if the specific rate constants at two different temperatures are known, E_a can be readily evaluated or when E_a and specific rate constant at one temperature are known, then specific rate constant at any other temperature can be calculated.

Problem 17.9. Benzene diazonium chloride decomposes in the presence of water according to first order kinetics. If the velocity constant at 25°C is 2.8×10^{-3} min^{-1}, and the activation energy is 11.9 kcal mol^{-1} find the velocity constant at 35°C.

Solution. We know that

$$\log \frac{k_2}{k_1}=\frac{E_a}{2.303R}\left(\frac{T_2-T_1}{T_2T_1}\right)$$

Here $E_a=11.9,\ R=1.987$

$k_1=2.8\times10^{-3}$, $T_1=273+25=298$ K

$k_2=?$ $T_2=273+35=308$ K

Therefore,

$$\log \frac{k_2}{2.8\times10^{-3}}=\frac{11.9}{2.303\times1.987}\left(\frac{308-298}{308\times298}\right)$$

or

$$k_2=5.37\times10^{-3}\ \text{min}^{-1}.$$

Problem 17.10. Trichloroacetic acid in aniline solvent (acting as catalyst) decomposes to give chloroform and carbon dioxide. The rate constant for this first order reaction is 4.0×10^{-5} min^{-1} at 25°C and 8.0×10^{-4} min^{-1} at 45°C. Calculate the energy of activation for this reaction.

Solution. Since

$$\log \frac{k_2}{k_1}=\frac{E_a}{2.303R}\left(\frac{T_2-T_1}{T_2T_1}\right)$$

Here $k_1=4.0\times10^{-5}$, $T_1=273+25=298K$

$k_2=8.0\times10^{-4}$, $T_2=273+45=318K$

$E_a=?$ $R=1.987$

Therefore

$$\log\frac{8.0\times10^{-4}}{4.0\times10^{-5}}=\frac{E_a}{2.303\times1.987}\left(\frac{318-298}{318\times298}\right)$$

or $E_a=27.6$ kcal mol^{-1}.

17.9. ENERGY OF ACTIVATION

Appearance of E_a factor in the Arrhenius equation leads to the fact that before reaction occurs, molecules must be activated, *i.e.*, they possess energy in excess of a certain amount. These activated molecules will then collide and lead to the reaction. Collisions between molecules which are not activated, will be of no use and no reaction will take place. The minimum energy which the molecules must absorb before the reaction can take place is known as the 'energy of activation'.

It follows from the concept of activation that reactants are not directly converted into products. The molecules first acquire energy to form an activated complex and then this activated complex decomposes into products at a definite rate as given below:

Reactants $\rightleftharpoons$ Activated State $\longrightarrow$ Products

In other words, there exists an energy barrier between the reactants and products. If the reactant molecules can cross this energy barrier, they will be converted into products. This can readily be understood by the energy diagram as shown in Fig. 17.7 in which the energy of the reactant molecules is plotted versus Reaction coordinate (rate of reaction).

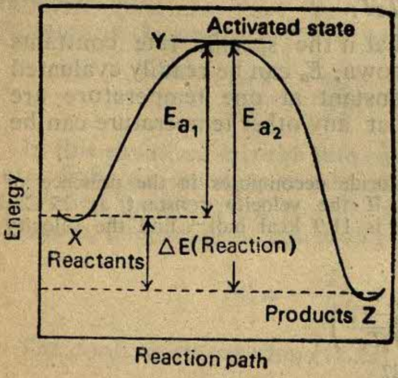


Fig. 17.7. Energy of activation.

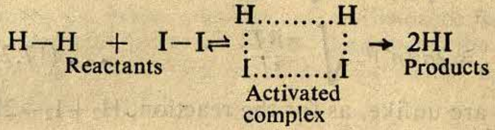
It is clear from this figure that energy equal to E_{a_1} must be absorbed by the reactants, X, to reach the activated state, Y. E_{a_1} is thus the energy of activation of the process $X\rightarrow Z$ and is equal to the difference in energy possessed by the molecules in the activated state and average energy of the reactants, *i.e.*, $E_{a_1}=E_y-E_x$. E_{a_2} is the energy released when the activated complex decomposes into products or this can also be taken as the energy of activation of the reverse process $Z\rightarrow X$ and is given by $E_{a_2}=E_y-E_z$.

Therefore, the difference in energy, ΔE, of the reaction is given by

$$\begin{aligned}\Delta E(\text{reaction}) &= E_{a_1} - E_{a_2} \\ &= E_y - E_x - E_y + E_z \\ &= E_z - E_x \qquad \ldots (17.26)\end{aligned}$$

This difference is also the heat of reaction at constant volume (from Thermodynamics). This means that activation energy E_{a_1} must be added to the molecules of the reactants in order to bring them in the activated state and the energy E_{a_2} is given out when molecules in the activated state go to products. If $E_{a_1} > E_{a_2}$, then ΔE (reaction) is *a* +ve quantity and the reaction is endothermic. If $E_{a_1} < E_{a_2}$, ΔE (reaction) is −ve and the reaction is exothermic. Thus the concept of energy of activation finds support from Thermodynamics.

According to the arguments given above, the reaction $H_2 + I_2 = 2HI$ takes place as follows:



$$\underset{\text{Reactants}}{H{-}H \;+\; I{-}I} \rightleftharpoons \underset{\substack{\text{Activated}\\\text{complex}}}{\begin{matrix} H \cdots\cdots\cdots H \\ \vdots \qquad\quad \vdots \\ I \cdots\cdots\cdots I \end{matrix}} \rightarrow \underset{\text{Products}}{2HI}$$

17.10. COLLISION THEORY OF REACTION RATES

In the Collision Theory, as is obvious from the name, a reaction takes place only if the molecules of the reactants collide. If collision is a necessary cause for the reaction to occur, then the rate of the reaction should be equal to the number of collisions per unit time between reactant molecules. But actually this is not the case. The number of collisions is found to be much large. This discrepancy can be explained in terms of "energy of activation" as already discussed. Thus only those collisions will lead to a reaction in which molecules possess energy in excess of the normal value so that at the moment of impact, the rearrangement of atoms can occur with a minimum expenditure of energy and time. All other collisions will lead to no reaction. Hence, the velocity of the reaction is given by the number of molecules colliding/c.c./sec and the fraction of these that possess sufficient energy of activation.

Consider a bimolecular reaction

$$A + B \longrightarrow \text{Products}$$

According to Collision Theory, the rate (k) of this reaction is given by

$$k = Zq \qquad \ldots (17.27)$$

where Z is the number of collisions per second between molecules and q the fraction of the molecules which are activated.

If the reaction is gaseous, the values of Z and q can be determined with the aid of the Kinetic Theory of gases.

According to this theory, the number of collisions per c.c. per sec. between like molecules of a gas as for the reaction, $2HI \rightarrow H_2 + I_2$, is given by

$$Z_{11} = \tfrac{1}{2}\sqrt{2}.\pi.\sigma^2.v(n')^2 \qquad \ldots (17.28)$$

where σ is the collision diameter of the molecules, v is the average velocity of the molecules in cm/sec and n' is the number of molecules per c.c. The value of v is given by

$$v = \sqrt{\frac{8RT}{\pi M}}$$

Substituting this value in equation (17.28), we have

$$Z_{11} = \frac{1}{\sqrt{2}}.\pi\sigma^2.\sqrt{\frac{8RT}{\pi M}}.(n')^2$$

$$= 2\sigma^2(n')^2.\sqrt{\frac{\pi RT}{M}} \qquad \ldots (17.29)$$

When the two molecules are unlike, as for the reaction, $H_2 + I_2 \rightarrow 2HI$ then $Z = Z_{12}$ and is given by

$$Z_{12} = n_1'n_2'(\sigma_{12})^2.\sqrt{\frac{8\pi RT}{\mu}} \qquad \ldots (17.30)$$

where $\sigma_{12} = \left(\frac{\sigma_1 + \sigma_2}{2}\right)$ is the mean collision diameter of the molecules, $\mu = \frac{M_1 M_2}{M_1 + M_2}$ is the reduced mass (M_1 and M_2 are the molecular weights of the two different molecules) and n_1' and n_2' are the number of molecules of each type per c.c. at temperature T.

The fraction of the molecules, q, having the necessary energy of activation is given by

$$\frac{n'^*}{n'} = e^{-\frac{E_a}{RT}} \qquad \ldots (17.31)$$

(Boltzmann equation for Maxwell distribution law of molecular velocities)

where n'^* is the number of activated molecules possessing an energy E_a out of total number of molecules n'/c.c. of a gas at temperature T.

(The only type of energy possessed by the molecules is assumed to be translational energy of motion).

Therefore, expression 17.27 for the rate constant becomes

$$k = Z.e^{-\frac{E_a}{RT}} \qquad \ldots (17.32)$$

where Z is given by equation (17.29) for like molecules or by equation (17.30) for unlike molecules.

This theoretical equation can be tested by comparing the calculated value of k with the experimental value for a number of reactions.

Consider the reaction $2HI(g) \rightarrow H_2(g) + I_2(g)$ at 556K. The quantity of the HI gas is 1 mole per litre.

The energy of activation (E_a) for this reaction at 556K is found to be 44,000 calories. For HI, $\sigma = 3.5 \times 10^{-8}$ cm., $M = 127.9$ and since 1 mole of a gas contains 6.023×10^{23} molecules/litre, therefore, the number of molecules/cc. is 6.023×10^{20}.

Substituting these values in equation (17.29) and solving, the result is

$$Z_{11} = 3.0 \times 10^{31}$$

Since Z_{11} is the number of collision/cc./sec. and two molecules are involved for a collision, therefore, the number of molecules colliding/cc./sec is double of this value *i.e.*, 6.0×10^{31} molecules.

Again, q for HI is given by

$$q = e^{-Ea/RT}$$

$$= e^{\frac{-44,000}{1.987 \times 556}}$$

$$= 5.2 \times 10^{-18}$$

Hence,

$$k = Z.q$$

$$= 6.0 \times 10^{31} \times 5.2 \times 10^{-18}$$

$$= 3.1 \times 10^{14} \text{ molecules reacting/cc./sec.}$$

If this value is multiplied by 1000 and divided by Avogadro number, we get the number of moles reacting per litre.

Therefore,

$$k = \frac{3.1 \times 10^{14} \times 1000}{6.023 \times 10^{23}}$$

$$= 5.2 \times 10^{-7} \text{ moles/litre/sec.}$$

The experimental values of k for this reaction is found to be 3.5×10^{-7} mols/litre/sec.

Agreement between the two values is fairly good. Although collision theory in the case of dissociation of hydrogen iodide and many other bimolecular reactions has been remarkably successful but for many reactions, both in gas phase and in solution, the calculated and observed values differ considerably. For example, for the reaction in which two molecules of ethylene combine, the discrepancy is a factor of about 2,000 while in the reaction between carbonyl sulphide and water vapor at about 300°C and many other reactions, the results calculated from collision theory are too high by factors ranging from 10^5 up to 10^9.

These discrepancies are due to the fact that the rate of reaction was calculated on the assumption that the molecules of the reactants behave as rigid spheres and activation energy is translational in nature. Although for simple molecules such as hydrogen iodide, hydrogen, and iodine, this assumption is fairly correct and good results are obtained but for more complex molecules, the approximation of rigid spheres is not valid and thus there is no reason to ignore energy contributions from rotational and vibrational motion which are in addition to the translation motion. If rotational and vibrational energies are also taken into consideration, the calculated results obtained are slightly better.

Thus, theoretical equation (17.32) is modified as

$$k = PZe^{-E_a/RT} \qquad \ldots (17.32a)$$

where P is called the *probability factor* or *steric factor*. The factor P is a measure of discrepancy between simple collision theory and the experimental results and may have values in the range of unity (when reactions obey the collision theory) to about 10^{-9} for slow reactions. It was also suggested that for slow reactions, collisions between those activated molecules of the reactants will result in reaction which have preferred critical orientation. Thus P is also a measure of the geometrical requirements that must be met when activated colliding molecules are to interact. Due to these factors, the value of probability factor may become as low as 10^{-3}—10^{-4} but it is doubtful whether these factors can explain the value of P lower than 10^{-4}.

Weaknesses of the Collision Theory. In recent years, some drawbacks of the Collision Theory have become apparent. The two main drawbacks are:

(*i*) Calculated value of P from the structures and properties of the reacting molecules is not in complete agreement.

(*ii*) Abnormally high values of the rate constants that are sometimes observed cannot be properly explained on the basis of the arguments given above.

17.11. THE TRANSITION-STATE THEORY OF REACTION RATES

This theory, which is also known as the *Theory of Absolute Reaction Rates*, attempts to explain rates on the basis of Thermodynamics and was developed by Eyring. According to this theory, molecules of the reactants before undergoing reaction must form an activated complex which is in thermodynamic equilibrium with the molecules of the reactants. The activated complex, the energy of which is higher than both reactants and products, is treated as a molecule and does not differ from ordinary molecules, except in one respect—it has transient existence and decomposes at a definite rate to form the products of the reaction. The rate of the reaction depends on two factors—(*i*) the concentration of the activated complex, and (*ii*) the rate at which the activated complex dissociates into products.

Thus, according to this theory, a reaction proceeds as follows:

$$\text{Reactants} \rightleftharpoons \text{Activated State} \rightarrow \text{Products}$$

Consider a simple bimolecular reaction between the molecules *A* and *B*. This reaction is represented as follows:

$$\underset{\text{Reactions}}{A+B} \rightleftharpoons \underset{\substack{\text{Activated}\\ \text{complex}}}{[A.B]^{\ddagger}} \xrightarrow{k} \text{Products}$$

(the double dagger symbol ‡ is used to denote activated state)

On the basis of these ideas, Eyring derived an equation for the specific rate (k) of any reoction, namely

$$k=\frac{RT}{Nh}\,K^{\ddagger} \qquad \ldots (17.33)$$

where R is the gas constant in ergs mole^{-1} deg^{-1}, T is the absolute temperature, N is the Avogadro's Number, h is the Planck's constant ($h=6.625\times10^{-27}$ erg-sec.) and $K^{\ddagger}$ is the equilibrium constant of the equilibrium between the activated complex and the reactants.

From thermodynamics, the constant $K^{\ddagger}$ can be interpreted in terms of the free energy of activation $\triangle G^{\ddagger}$, the enthalpy of activation $\triangle H^{\ddagger}$ and the entropy of activation $\triangle S^{\ddagger}$ as follows:

$\triangle G,^{\ddagger}$ $\triangle H^{\ddagger}$ and $\triangle S^{\ddagger}$ represent the difference between the values of the respective thermodynamic functions for the activated complex and the reactants, all substances being in their standard states, *i.e.*, activity$=1$).

Writing the expression for $K^{\ddagger}$ in terms of $\triangle G^{\ddagger}$, we have

$$\triangle G^{\ddagger}=-RT\,ln\,K^{\ddagger} \qquad (\text{since } \triangle G=-RT\,ln\,K)$$

or

$$ln\,K^{\ddagger}=-\frac{\triangle G^{\ddagger}}{RT} \qquad \ldots (17.34)$$

For the reaction at a temperature T, $\triangle G^{\ddagger}$ can be written in terms of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ by the equation

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad \ldots (17.35)$$

Substituting this value in equation (17.34)

$$\ln K^{\ddagger} = -\frac{\Delta H^{\ddagger} - T\Delta S^{\ddagger}}{RT} \qquad \ldots (17.36)$$

or

$$K^{\ddagger} = e^{-\frac{\Delta H^{\ddagger} - T\Delta S^{\ddagger}}{RT}}$$

$$= e^{\frac{\Delta S^{\ddagger}}{R}} . e^{\frac{-\Delta H^{\ddagger}}{RT}} \qquad \ldots (17.37)$$

Substituting this value of $K^{\ddagger}$ in equation (17.33), we get

$$k = \frac{RT}{Nh} e^{-\frac{\Delta G^{\ddagger}}{RT}} \qquad \ldots (17.38)$$

or

$$k = \frac{RT}{Nh} e^{\frac{\Delta S^{\ddagger}}{R}} . e^{-\frac{\Delta H^{\ddagger}}{RT}} \qquad \ldots (17.39)$$

Since the activated complex has got transient existence only, therefore, it is not possible to determine its thermodynamic properties $\Delta G^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ by direct measurement. However, some useful information can be obtained from equations (17.38) and (17.39). Since the factor, $\frac{RT}{Nh}$, in equations (17.38) and (17.39) is a universal constant for a given temperature and has no reference either to the reactants or the activated state, therefore, from equation (17.38), the specific rate of the reaction at a constant temperature depends on $\Delta G^{\ddagger}$, the free energy of activation. *The higher the value of* $\Delta G^{\ddagger}$ *, the slower the reaction rate at a constant temperature.* This is a conclusion of outstanding significance.

If equation (17.39) is compared with the Arrhenius equation, $k = A\, e^{-\frac{E_a}{RT}}$, we see that the frequency factor A is equal to $\frac{RT}{Nh} . e^{\frac{\Delta S^{\ddagger}}{R}}$ and $\Delta H^{\ddagger}$ is equivalent to the energy of activation, Ea.

Thus, A can be evaluated in terms of $\triangle S^{\ddagger}$ and $\triangle H^{\ddagger}$ can be calculated in terms E_a

For reactions involving solids and liquids,

$$E_a = \triangle H^{\ddagger} \qquad \ldots (17.40)$$

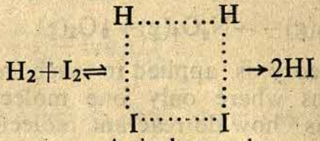
$(\because \triangle H^{\ddagger} = E_a + \triangle (PV)^{\ddagger}$
For solids and liquids

$\triangle (PV)^{\ddagger}$ is negligibly small).

For reactions involving gases, a change in the number of moles, $\triangle n^{\ddagger}$, takes place when reactants from the activated complex and

$$\triangle H^{\ddagger} = E_a + \triangle n^{\ddagger} \, . \, RT \qquad \ldots (17.41)$$

For bimolecular reactions *e.g.*,



$$H_2 + I_2 \rightleftharpoons \begin{matrix} H \cdots\cdots H \\ \vdots \quad\quad \vdots \\ I \cdots\cdots I \end{matrix} \rightarrow 2HI$$

A single complex
moleucle

$$\triangle n^{\ddagger} = -1,$$

$$\triangle H^{\ddagger} = E_a - RT \text{ and so on.}$$

On comparing equation (17.39) with equation (17.32a) of the collision theory, we see that the probability factor can be interpreted in terms of entropy of activation, *i.e.*,

$$PZ = \frac{RT}{Nh} \, . \, e^{\frac{\triangle S^{\ddagger}}{RT}} \qquad \ldots (17.42)$$

Z, the number of collisions, is readily calculated and knowing the value of P, $\triangle S^{\ddagger}$ can be calculated.

Though for complex molecules, the collision theory fails, the theory of Absolute Reaction Rate is still successful. This is due to the presence of $\triangle S^{\ddagger}$ factor in the theory of Absolute Reaction Rate. It has been found that the value of $\triangle S^{\ddagger}$ is negative. The negative value of $\triangle S^{\ddagger}$ indicates that the formation of activated complex (which is more ordered than the molecules of the reactants) from the reactants is accompanied by a large decrease of entropy. Larger the complexity of the reacting molecules, greater will be the decrease in the value of entropy. This results in the smaller values of the quantity $e^{\frac{\Delta S^{\ddagger}}{R}}$ and since $\frac{RT}{Nh}$ is the same for all reactions, therefore, PZ value would be much less than the interpreted value.

17.12. THE COLLISION THEORY OF UNIMOLECULAR REACTIONS

The Collision Theory and the Transition State Theory, as discussed above, give a fairly satisfactory account only for bimolecular reactions. Both the theories stress that before a reaction takes place, collisions between molecules of the reactants must occur so that the reactant molecules can attain enough energy to react. It may lead to the conclusion that all gaseous reactions are of second order. However, a number of gaseous reactions were kinetically found to be of first order *e.g*, gaseous decomposition of N_2O_5.

$$N_2O_5(g) \longrightarrow N_2O_4(g) + \tfrac{1}{2}O_2(g)$$

When Collision Theory is applied to such reactions and other unimolecular reactions where only one molecule participates, the question that puzzles is "how do reactant molecules attain necessary energy of activation?" In case the molecules attain the necessary energy by collisions with other molecules, the collision rate will depend on the square of the concentration. This will make the reaction second order whereas it follows first order kinetics.

To explain this, Lindemann in 1922 proposed a mechanism by which reactant molecules could be activated by collisions and yet the reaction be of first order.

Consider a unimolecular reaction

$$A \longrightarrow \text{Products}$$

The molecule A decomposes into the products with a first order rate law

$$\frac{-dC_A}{dt} = k_1 C_A$$

In the reaction vessel containing molecules of A, the molecules are continually colliding with each other. As a result of these collisions, some of the molecules are activated *i.e.*, they attain energy higher than the average energy. It should be noted that the activated molecule in this case is a single reactant molecule and there is no activated complex which is made of two or more molecules. Lindemann assumed that there is a time lag between activation by collision and reaction *i.e.*, the activated molecule does not immediately decompose but moves around in the activated form for a short time. During this existence, the activated molecule can follow either of the two paths: (*i*) It may be deactivated by collision with energy poor molecule. This will lead to the formation of the normal reactant molecules, and (*ii*) it may decompose into products.

The whole idea can be represented by the mechanism as follows:

$$A+A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A+A^* \qquad \ldots (17.43)$$

$$A^* \xrightarrow{k_3} \text{Products} \qquad \ldots (17.44)$$

where A represents a normal molecule and A^* an activated molecule. k_1, k_2 and k_3 are the rate constants for the activation, deactivation and decomposition process respectively. Activation and deactivation processes are bimolecular reactions and decomposition process is a true unimolecular reaction.

The rate of disappearance of A into products is given by the last reaction and is expressed as

$$\frac{-dC_A}{dt}=k_3C_{\text{A}}^* \qquad \ldots (17.45)$$

To determine the concentration of activated molecules *i.e.*, C_{A}^* in terms of concentration of normal molecules, we make use of a postulate known as *Steady-state approximation*. According to this, it is assumed that once the reaction starts, a steady stage is reached in which the concentration of the activated molecules becomes very small and does not change much with time. Thus, according to Steady-state approximation.

$$\frac{dC_{\text{A}}^*}{dt}=0 \qquad \ldots (17.46)$$

Since A^* is formed in the first reaction with a rate $k_1C_{\text{A}}^2$ and is removed in the first reaction (reverse) with a rate $k_2C_AC_{\text{A}}^*$ and in the second reaction with a rate $k_3C_{\text{A}}^*$, we have

$$\frac{dC_{\text{A}}^*}{dt}=0=k_1C_A{}^2-k_2C_AC_{\text{A}}^* -k_3C_A^* \qquad \ldots (17.47)$$

or

$$k_1C_{\text{A}}^2=k_2C_A\,C_{\text{A}}^* +k_3C_{\text{A}}^*$$

Solving for C_{A}^*

$$C_{\text{A}}^*=\frac{k_1C_A{}^2}{k_2C_A+k_3} \qquad \ldots (17.48)$$

This equation expresses C_{A}^* in terms of C_A, the concentration of the normal molecules.

Substituting this value of $C_A{}^*$ into equation (17.45), we get

$$\frac{-dC_A}{dt}=\frac{k_1k_3C_A^2}{k_2C_A+k_3} \qquad \ldots (17.49)$$

Equation (17.49) has two limiting forms:

Case I. When the rate of decomposition of A^* is much faster than its rate of deactivation *i e.* $k_3C_A^* >> k_2C_AC_A^*$ or $k_3 >> k_2C_A$. Under this condition, k_2C_A in the denominator can be neglected in comparison to k_3 and hence equation (17.49) reduces to

$$\frac{-dC_A}{dt}=\frac{k_1k_3C_A^2}{k_3} \qquad \ldots (17.50)$$

$$=k_1C_A^2$$

This is an expression for second order. Thus, when the concentration (pressure) of A is very low, the reaction becomes a second order process. This corresponds to the situation that when C_A is very low, active molecules will have little chance of collision, will stay longer and chances of decomposition into products is much more.

Case II. When the rate of deactivation of A^* is much greater than its rate of decomposition, $k_2C_A >> k_3$ and equation (17.49) becomes

$$\frac{-dC_A}{dt}=\frac{k_1k_3}{k_2C_A}.\ C_A^2=k_2'C_A \qquad \ldots (17.51)$$

where $$k'_1=\frac{k_1k_3}{k_2}$$

This is an expression for the first order reaction. Thus, when the concentration (pressure) of A is very high, the reaction becomes a first order process. This corresponds to the situation that when C_A is high, the activated molecules will have greater chances of colliding with inactive molecules and thus become deactivated than of decomposition to give products *i.e.*, a very small fraction of the activated molecules will decompose to yield products.

Thus it is evident that in gaseous reactions, the second order kinetics changes to first order kinetics when pressure is increased. This change has been observed in many unimolecular gaseous decomposition reactions.

The Lindeman Theory of Unimolecular reactions has been found to be very successful and can satisfactorily explain many experiment.

17.13. KINETIC THEORY OF TERMOLECULAR REACTIONS

If collision theory is applied to termolecular reactions, it is observed that the rate constant calculated on the basis of triple collisions is much larger than the experimental value. In order to account for the mechanism of third order reactions, Trautz in 1916 suggested that true ternary collisions between molecules are very rare (roughly one triple collision for every 10,000 ordinary collisions). He regarded the termolecular reactions as taking place in two stages. For example, the interaction between NO and X_2 where X_2 may be Cl_2, Br_2, O_2 or H_2, namely

$$2NO+X_2 \rightarrow 2NOX$$

may be regarded as being taking place in the following two stages:

(*i*) $NO \ \ +X_2 \rightleftharpoons NOX_2$

(*ii*) $NOX_2+NO \underset{k_2}{\rightarrow} 2NOX$

According to this scheme, an equilibrium is set up in (*i*) for which the constant is

$$K=\frac{[NOX_2]}{[NO]\,[X_2]}$$

Then $$[NOX_2]=K[NO]\,[X_2] \qquad \ldots (17.52)$$

The overall rate of reaction is determined from step (*ii*) which is the slower reaction. The rate of this reaction is

$$\frac{d[NOX]}{dt}=k_2[NOX_2]\,[NO] \qquad \ldots (17.53)$$

Substituting equation (17.52) into equation (17.53), we get

$$\frac{d[NOX]}{dt}=k_2K[NO]^2[X_2] \qquad \ldots (17.54)$$

which is a third order reaction with constant $k_3=k_2\,K$.

The equilibrium assumption in step (*i*) also explains why the rate of termolecular reaction decreases with increase in temperature. Increase in temperature tends to dissociate NOX_2 with the result that the concentration of X_2 is lowered, and thus the rate of the reaction is reduced.

17.14. COMPLEX REACTIONS

There are many reactions both in nature and in the laboratory which do not take place strictly according to the equation derived. These reactions involve two or more side reactions in addition to the actual reactions and thus the kinetics of such reactions is complicated. The various complications are due to the following factors:

(*i*) Reversible or Opposing Reactions:

(*ii*) Consecutive Reactions; and

(*iii*) Side Reactions or Parallel Reactions.

(*i*) **Reversible or opposing reactions.** So far it has been assumed that a reaction takes place in the forward direction and does not reverse. But, it has been found that majority of the reactions are reversible and forward and reverse reactions take place simultaneously *e.g.*, oxidation of nitric oxide to nitrogen dioxide, hydrolysis of ethyl acetate in aqueous solutions etc. These reactions take place as:

$$2NO+O_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2NO_2$$

(k_1 is the rate constant for the forward reaction and k_2 is the rate constant for the backward reaction)

$$CH_3COOC_2H_5+H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CH_3HOOC+C_2H_5OH$$

(The symbol $\rightleftharpoons$ indicates that the reaction is reversible)

Consider a simplest case of this type in which both forward and reverse reactions are of first order:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \qquad \ldots (17.55)$$

k_1 and k_{-1} are the first order rate constants for the forward and reverse reactions respectively. Initially at $t=0$, let 'a' be the concentration of A and there will be no B. After time t, if x is the amount of A transformed into B, the concentrations of A and B will be $(a-x)$ and x respectively.

Therefore, the rate of the reaction will become

$$\frac{dx}{dt}=k_1\,(a-x)-k_{-1}x \qquad \ldots (17.56)$$

where $k_1\,(a-x)$ is the actual rate for the forward reaction and $k_{-1}x$ is the rate for the reverse reaction.

At equilibrium, the two rates are equal. If x_e is the amount of the product formed at equilibrium, then

$$k_1\,(a-x_e)=k_{-1}x_e$$

or

$$k_{-1}=\frac{k_1(a-x_e)}{x_e} \qquad \ldots (17.57)$$

Substituting this value of k_{-1} in equation (17.56),

$$\frac{dx}{dt}=k_1\,(a-x)-\frac{k_1x(a-x_e)}{x_e}$$

$$=\frac{k_1a(x-x_e)}{x_e} \qquad \ldots (17.58)$$

Integrating this equation in the limits that at $t=0$, $x=0$ and at time t, $x=x$, we get

$$\frac{k_1a}{x}=\frac{1}{t}ln\,\frac{x_e}{x_e-x} \qquad \ldots (17.59)$$

Therefore, if x_e is known, the specific rate constant for the forward reaction can be calculated.

Similarly, expressions for second order opposing reactions can also be obtained.

(*ii*) **Consecutive reactions** These are those reactions in which the product of one reaction becomes the reactant for the other reaction *e.g.*,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

In this reaction, A is the original reactant and gives the product B at the rate constant k_1. This product formed further reacts to give the substance C at some other rate constant k_2. The kinetics of such a reaction is determined by the slowest step. In the above reaction, if first reaction is faster than the second reaction, the kinetics will be determined by the second reaction. In general, it can be stated that if a reaction takes place in series, then the slowest reaction will be the rate-determining reaction.

Let a be the initial concentration of A, x the amount of it decomposed after time t and y the amount of C formed at the same time. Thus at time t, we have

concentration of A, $C_A = a-x$ ... (17.60)

concentration of C, $C_C = y$ ... (17.61)

and concentration of B, $C_B = x-y$ ... (17.62)

(Because the total amount of B formed is x and y of it decomposes to form C)

Therefore, rate of disappearance of A is given by

$$\frac{dx}{dt} = k_1(a-x) \qquad \ldots (17.63)$$

and that of B is given by $\frac{dy}{dt} = k_2(x-y)$ ... (17.64)

(This is also the rate of formation of C)

To show the variation of concentrations of A, B and C with time, equation (17.63) is integrated in the limits that $x=a$ when $t=0$ and $x=x$ at time t. This gives

$$C_A = (a-x) = ae^{-k_1t} \qquad \ldots (17.65)$$

Substituting the value of x from equation (17.65) into equation (17.64) and then integrating the latter equation we get,

$$C_B = (x-y) = a\,\frac{k_1}{k_2-k_1}\,(e^{-k_1t} - e^{k_2t}) \qquad \ldots (17.66)$$

Knowing C_A and C_B at time t, C_C can be found.

Its value comes out to be

$$C_C=\frac{a}{k_2-k_1}\left[\ (k_2-k_2.\ e^{-k_1t})-(k_1-k_1e^{-k_2t})\ \right] \qquad \ldots (17.67)$$

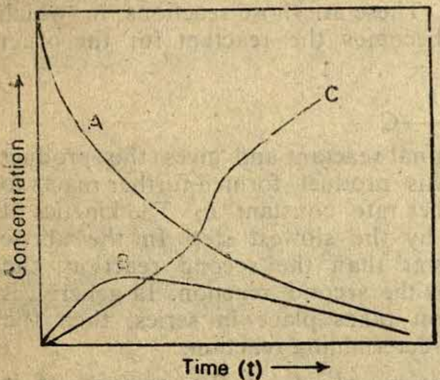


Fig. 17.8. Concentration versus time in consecutive reactions.

The general manner in which C_A, C_B and C_C vary with time t is shown by the curves in Fig. 17.8.

It is clear from the various curves that concentration of A decreases and that of C increases continuously while the concentration of B passes through a maximum and then begins to decrease with time.

Examples

1. *Pyrolysis of acetone*

This takes place in two steps:

(*a*) $CH_3COCH_3 \longrightarrow CH_2{=}CO+CH_4$; and

(*b*) $CH_2{=}CO \longrightarrow \frac{1}{2}C_2H_4+CO$

2. *Decomposition of sodium hypochlorite in alkaline solutions*

(*a*) $2NaClO \longrightarrow NaCl+NaClO_2$; and

(*b*) $NaClO_2+NaClO \longrightarrow NaCl+NaClO_3$

(*iii*) **Side reactions**. These are those reactions in which the reactant gives the products in more than one way. The reaction which gives the maximum quantity of the product is called the main reaction and the others yielding poor amount of the products are called the side reactions. Side reactions are quite common in organic chemistry, as shown in Fig. 17.9. k_1 is the rate constant for the main reaction and k_2 the rate constant for the side reaction.

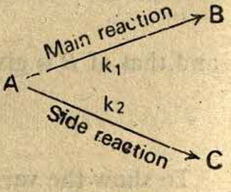


Fig. 17.9.

If a is the initial concentration of A and x is the amount of it that decomposes into B and C at time t, the rate of disappearance of A is given by

$$\frac{dx}{dt}=(k_1+k_2)\ x \qquad \ldots (17.68)$$

and the rate of formation of B and C is given by

$$\frac{d[B]}{dt}=k_1x \qquad \ldots (17.69)$$

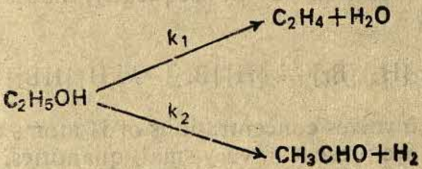
and $$\frac{d[C]}{dt}=k_2x \qquad \ldots (17.70)$$

Ratio of equations (17.69) and (17.70) gives

$$\frac{d[B]}{d[C]}=\frac{k_1}{k_2} \qquad \ldots (17.71)$$

With the help of equations (17.68) and (17.71), k_1 and k_2 can be calculated.

Example: Alcohol can be dehydrated to olefins as well as dehydrogenated to aldehyde:



17.15. CHAIN REACTIONS

There are some chemical reactions which take place by a series of successive processes involving the formation of free atoms and radicals. The kinetic laws for such reactions are considerably complex. A well known example of these types of reactions is the hydrogen-bromine reaction. The stoichiometry for this reaction is

$$H_2+Br_2 \longrightarrow 2HBr$$

but it does not follow the simple rate expression

$$\frac{d[HBr]}{dt}=k[H_2][Br_2]$$

analogous to that followed in the hydrogen-iodine reaction but follows the following empirical rate equation given by Bodenstein and Lind in 1906:

$$\frac{d[HBr]}{dt}=\frac{k[H_2][Br_2]^{1/2}}{1+k'\frac{[HBr]}{[Br_2]}} \qquad \ldots (17.72)$$

k and k' are constants at a given temperature and parentheses indicate the concentration of the species. The appearance of the term [HBr] in the denominator implies that the velocity of the reaction is decreased by the product, HBr, and this product acts as an inhibitor of the reaction.

The complexity of equation (17.72) could not be explained until 1919 when Christiansen, Herzfeld, and Polanyi independently and almost simultaneously solved the problem. They proposed a chain of reactions with the following steps:

$$(1)\ \mathrm{Br_2} \xrightarrow{k_1} \mathrm{2Br} \qquad \text{Chain initiation}$$

$$\left.\begin{array}{l}(2)\ \mathrm{Br} + \mathrm{H_2} \xrightarrow{k_2} \mathrm{HBr} + \mathrm{H} \\ (3)\ \mathrm{H} + \mathrm{Br_2} \xrightarrow{k_3} \mathrm{HBr} + \mathrm{Br}\end{array}\right\} \text{Chain propagation}$$

$$(4)\ \mathrm{H} + \mathrm{HBr} \xrightarrow{k_4} \mathrm{H_2} + \mathrm{Br} \qquad \text{Chain inhibition}$$

$$(5)\ \mathrm{2Br} \xrightarrow{k_5} \mathrm{Br_2} \qquad \text{Chain termination}$$

According to this mechanism, HBr is formed in reactions (2) and (3) and removed in reaction (4). Consequently, the rate of formation of HBr is given by

$$\frac{d[\mathrm{HBr}]}{dt} = k_2[\mathrm{H_2}]\,[\mathrm{Br}] + k_3[\mathrm{H}]\,[\mathrm{Br_2}] - k_4[\mathrm{H}]\,[\mathrm{HBr}] \qquad \ldots (17.73)$$

This expression involves concentrations of H atoms and Br atoms. Since these atoms are present in very small quantities, their concentrations cannot be directly measured. Thus equation (17.73) cannot be solved unless the concentrations of these atoms are expressed in terms of the concentrations of the molecules H_2, Br_2, and HBr. In order to remove this difficulty, it is assumed that the atoms H and Br are short lived intermediates and the steady state principle can be applied to them. Thus we get

$$\frac{d[\mathrm{H}]}{dt} = k_2[\mathrm{Br}]\,[\mathrm{H_2}] - k_3[\mathrm{H}]\,[\mathrm{Br_2}] - k_4[\mathrm{H}]\,[\mathrm{HBr}] = 0 \qquad \ldots (17.74)$$

$$\frac{d[\mathrm{Br}]}{dt} = k_1[\mathrm{Br_2}] + k_3[\mathrm{H}]\,[\mathrm{Br_2}] + k_4[\mathrm{H}]\,[\mathrm{HBr}] - k_2[\mathrm{Br}]\,[\mathrm{H_2}] - k_5[\mathrm{Br}]^2 = 0 \qquad \ldots (17.75)$$

Solving these two equations simultaneously, we get

$$[\mathrm{Br}] = \left(\frac{k_1[\mathrm{Br_2}]}{k_5}\right)^{1/2} \qquad \ldots (17.76)$$

and

$$[\mathrm{H}] = \frac{k_2(k_1/k_5)^{1/2}[\mathrm{H_2}]\,[\mathrm{Br_2}]^{1/2}}{k_3[\mathrm{Br_2}] + k_4[\mathrm{HBr}]} \qquad \ldots (17.77)$$

Substituting these values for [H] and [Br] into equation (17.73) and rearranging, we get

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{2k_2(k_1/k_5)^{1/2}[\mathrm{H_2}]\,[\mathrm{Br_2}]^{1/2}}{1 + (k_4/k_3)\,\dfrac{[\mathrm{HBr}]}{[\mathrm{Br_2}]}} \qquad \ldots (17.78)$$

This equation is in agreement with equation (17.72) but now the constants k and k' are expressed as composites of constants for step reactions in succession.

A reaction like the above is an example of a chain reaction. Inspection of steps (1) to (5) for the hydrogen-bromine reaction leads to a number of points of interest in the mechanism. The reaction is initiated by thermal dissociation of a bromine molecule into bromine atoms. The introduction of bromine atoms produces a large number of molecules of hydrogen bromide through the sequence of reactions (2) and (3). These two stages repeat themselves until the reactants are used up. These reactions are *chain-propagating reactions*. Step (4) accounts for the observed inhibition by HBr; since the product HBr is removed by this step, there is a decrease in the rate of formation of HBr. Step (5) results in removal of bromine atoms, and hence in chain termination. In some cases, chain termination may take place by collisions of chain propagators with the walls of the reacting vessel.

In some chain reactions, free radicals such as CH_3, C_2H_5, or CH_3CO, act as chain carriers. Consider, for example, the thermal decomposition of acetaldehyde, namely,

$$CH_3CHO \rightarrow CH_4 + CO.$$

The following mechanism has been proposed for this reaction:

$$(1)\ CH_3CHO \xrightarrow{k_1} CH_3 + CHO \qquad \text{Chain initiation}$$

$$\left.\begin{array}{l}(2)\ CH_3CHO + CH_3 \xrightarrow{k_2} CH_4 + CH_3CO \\ (3)\ CH_3CO \xrightarrow{k_3} CH_3 + CO\end{array}\right\} \text{Chain propagation}$$

$$(4)\ CH_3 + CH_3 \xrightarrow{k_4} C_2H_6 \qquad \text{Chain termination}$$

Step (1) initiates the chain, steps (2) and (3) propagate the chain and step (4) terminates the chain. Applying the steady-state principle to the radicals CH_3 and CH_3CO, we get

$$\frac{d[CH_3]}{dt} = k_1[CH_3CHO] + k_3[CH_3CO] - k_2[CH_3CHO][CH_3] - k_4[CH_3]^2 = 0 \quad \ldots (17.79)$$

and
$$\frac{d[CH_3CO]}{dt} = k_2[CH_3CHO][CH_3] - k_3[CH_3CO] = 0 \quad \ldots (17.80)$$

From these two equations, we get

$$k_1[CH_3CHO] = k_4[CH_3]^2$$

or
$$[CH_3] = (k_1/k_4)^{1/2}\,[CH_3CHO]^{1/2} \quad \ldots (17.81)$$

The overall rate of reaction is determined by the production of CH_4 in step (4). The rate equation is

$$\frac{d[CH_4]}{dt} = k_2[CH_3CHO][CH_3] \quad \ldots (17.82)$$

Substituting the value of $[CH_3]$ from equation (17.81) into equation (17.82), we get

$$\frac{d[CH_4]}{dt} = k_2\left(\frac{k_1}{k_4}\right)^{\frac{1}{2}} [CH_3CHO]^{3/2} \quad \ldots (17.83)$$

The free-radical scheme thus predicts the reaction to be of the $\frac{3}{2}$ order. This is in agreement with the experimental data which shows a first order reaction gradually becoming a second order reaction.

Free radical chains play an important role in the polymerization of many unsaturated compounds, such as ethylene, styrene and vinyl compounds, to produce materials of industrial importance.

17.16. BRANCHING CHAINS, EXPLOSIVE REACTIONS

In the chain reactions discussed above, each propagation phase produces a molecule of product and one chain carrier. This is referred to as a *stationary state*. In some reactions, it has been frequently observed that more than one chain carrier is produced from the original one in each propagating phase. This results in *branching* (or *nonstationary*) *chain*, in which the number of chain carriers increase rapidly. The reaction then takes place very rapidly and explosion is said to occur. (In fact, explosions do occur if chain carriers are produced more quickly than they can be removed.) A reaction mechanism that involves branching reactions is known as *branching chain process*.

One of the consequences of the formation of branching chains is the phenomenon of explosion limit discovered by Hinshelwood and his co-workers in 1928. It is exhibited by a number of oxidation reactions, *e.g.*, of hydrogen, carbon monoxide, carbon disulphide and phosphine.

Consider the reaction between hydrogen and oxygen. This reaction takes place at a conveniently measurable speed between the temperature range of 450°C and 600°C. Below this range, the rate is very slow, but above this range, the reaction takes place extremely rapidly, *i.e.*, becomes explosive. If the mixture of H_2 and O_2 in the ratio 2 : 1 is maintained at 550°C and at a pressure of about 2 mm, a steady homogeneous reaction occurs. If the pressure is gradually raised, the rate increases. At a certain critical pressure of few millimetres, the reaction suddenly becomes explosive. This is referred to as first (lower) explosion limit. The explosive reaction persists with further increase of pressure but above a pressure of 50 mm at 500°C, there is no longer an explosion and the reaction rate is normal. If the pressure is further increased at about 100 mm, a condition is once again reached at which the reaction is very rapid and explosion reoccurs. This is referred to as second (upper) explosion limit. At about 200 mm pressure, the reaction is again steady. At still higher pressures, a third limit is achieved. This behaviour is displayed in Fig. 17.10.

In order to explain the existence of explosion limits, the branching chain mechanism is utilised. At very low pressures, the chain carriers diffuse quickly to the walls of vessel and are destroyed at the surface, thus terminating the chain. The rate of the reaction is, therefore, slow. As the pressure is increased, rate of formation of chain carriers exceed their rate of destruction; the reaction rate then increases enormously and explosion occurs. This represents lower

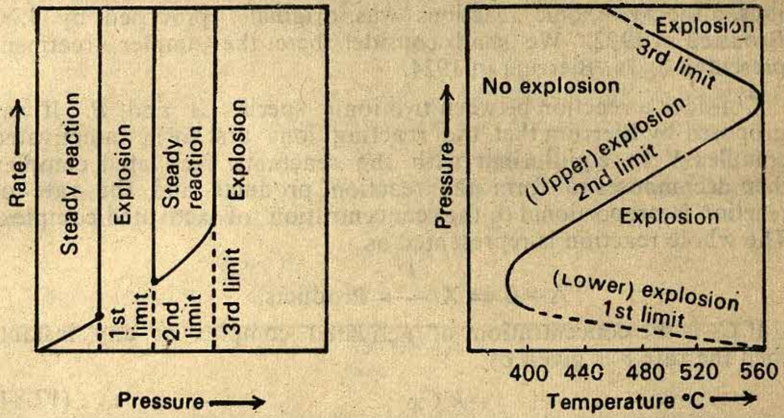


Fig. 17.10. Explosion limits.

explosion limit which depends on the size and material of the reaction vessel. Further increase of pressure favours destruction of chain carriers by their mutual collisions in the interior of the gas. Eventually, the upper explosion limit is reached when destructive collisions in the gas phase exceed the chain branching. The reaction becomes non-explosive in character and goes smoothly. At still higher pressures, represented by the third explosion limit, the reaction is again so fast that the conditions are no longer isothermal and reaction passes over into a *thermal explosion*. In a thermal explosion, since the heat liberated is not dissipated, the temperature of the reaction system rises rapidly and the rate of reaction increases practically without bound.

Taking into consideration the views expressed above, the following mechanism is suggested for the hydrogen-oxygen reaction:

(1) $H_2 \rightarrow 2H$ Chain initiation

$$\left.\begin{array}{ll}(2)\ H+O_2 & \rightarrow OH+O\\ (3)\ O+H_2 & \rightarrow OH+H\end{array}\right]\ \text{Chain branching}$$

(4) $OH+H_2 \rightarrow H_2O+H$ Chain propagation
(5) $H+\text{wall} \rightarrow$ Destruction
(6) $OH+\text{wall} \rightarrow$ Destruction
(7) $O+\text{wall} \rightarrow$ Destruction.

17 17. INFLUENCE OF IONIC STRENGTH

The specific rate constants of reactions in solution involving either non-electrolytes or non-electrolytes and ions generally remain unaffected by the presence of elecrolytes. On the other hand, rates of reactions taking place between ions are very much affected by varying the ionic strength of the solution. In order to explain the influence of ionic strength on the rates of reactions between two ions, a theory of ionic reactions was originally proposed by J.N. Bronsted in 1922. We shall consider here the simpler treatment presented by N. Bjerrum in 1924.

Consider a reaction between two ionic species *A* and *B*. It was proposed by Bjerrum that the reacting ions first form an activated complex *X* in equilibrium with the reactants. Activated complex then decomposes to form the reaction products and the rate of reaction is proportional to the concentration of activated complex. The whole reaction is represented as

$$\mathrm{A+B} \rightleftharpoons \mathrm{X} \xrightarrow{k'} \text{Products.}$$

If C_X is the concentration of activated complex at any instant, then the rate v is given by

$$v=k'C_X \qquad \ldots (17.84)$$

Since the activated complex is in equilibrium with the reactants, the thermodynamic equilibrium constant K is expressed as

$$K=\frac{a_X}{a_A a_B}=\frac{C_X}{C_A C_B}\cdot\frac{f_X}{f_A . f_B} \qquad \ldots (17.85)$$

where the a's are the activities, C's are the concentrations and f's are the activity coefficients of the various species. From equation (17.85), C_X is given by

$$C_X=K\, C_A C_B .\ \frac{f_A f_B}{f_x}$$

which on substitution into equation (17.84) gives rise to

$$v=k'KC_A C_B\ .\ \frac{f_A f_B}{f_x}$$

$$=\left(k_0\frac{f_A f_B}{f_x}\right)C_A C_B \qquad \ldots (17.86)$$

where $k_0=k'\,K$.

Equation (17.86) indicates that the experimentally evaluated constant k, as determined from the ordinary kinetic equation for a bimolecular reaction between A and B, namely

Rate of reaction, $v=\mathrm{k}C_A C_B$ $\qquad \ldots (17.87)$

is not the true reaction constant k_0 but involves also the activity coefficients of the reactants and the complex. Thus the experimental specific rate constant is given by

$$k=k_0\ \frac{f_A\, f_B}{f_x} \qquad \ldots (17.88)$$

Taking logarithms,

$$\log_{10} k=\log_{10} k_0+\log_{10}\frac{f_A\, f_B}{f_x} \qquad \ldots (17.89)$$

At infinite dilution, the activity coefficient on the right of equation (17.89) would be unity and its logarithm zero; hence, physically k_0 is the specific rate constant of the reaction between A and B extrapolated to infinite dilution. In general, the activity coefficients of charged reactants and complex vary with the ionic strength of the medium, and so the velocity constant will be a function of the ionic strength. This is referred to as the *primary salt effect* on reactions involving ions.

According to the Debye-Huckel Theory, the activity coefficient of an ion in aqueous solutions at 25°C is related to its valency Z and the ionic strength μ by the equation

$$\log_{10} f = -0.51\, Z^2 \sqrt{\mu} \qquad \ldots (17.90)$$

The ionic strength is defined by the equation

$$\mu = \frac{1}{2} \sum_i Zi^2\, Ci \qquad \ldots (17.91)$$

where Z_i is the valency of the ion and C_i its concentration, the summation being taken of all the ions in the solution.

Substituting equation (17.90) into equation (17.89) and simplifying, we get

$$\log_{10} k = \log_{10} k_0 - 0.51\, (Z_A^2 + Z_B^2 - Z_X^2) \sqrt{\mu} \qquad \ldots (17.92)$$

where Z_A, Z_B and Z_X are the charges carried by A, B and X respectively. Since $Z_X = Z_A + Z_B$, equation (17.92) reduces to

$$\log_{10} k = \log_{10} k_0 + 1.02\, Z_A Z_B \sqrt{\mu} \qquad \ldots (17.93)$$

According to equation (17.93), a plot of $\log_{10} k$ or of $\log_{10} k/k_0$ against $\sqrt{\mu}$ should give a straight line with a slope $1.02\ Z_A Z_B$. This agreement is confirmed when we consider Fig. 17.11.

This figure shows a plot of $\log_{10} k/k_0$ versus $\sqrt{\mu}$ for reactions of various types; the lines drawn are those predicted by equation (17.93), while the points are experimental results.

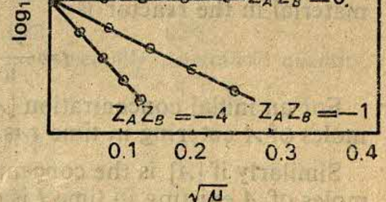


Fig. 17.11. Primary salt effect in ionic reactions of various type.

As can be seen from the figure, if one of reactants is a neutral molecule, $Z_A Z_B = O$, and the rate constant should be independent of the ionic strength. This is true for a reaction of the type.

$CH_3COOC_2H_5 + OH^- \rightarrow CH_3COO^- + C_2H_5OH$

(base-catalysed hydrolysis of ethyl acetate)

If Z_AZ_B is positive, as for the reactions

$$2[Co\,(NH_3)_5Br]^{2+}+Hg^{2+}+2H_2O=2[Co(NH_3)_5\,(H_2O)]^{+3}+Hg\,Br_2\;(Z_AZ_B=+4)$$

$$S_2O_8^{2-}+2I^-=I_2+2SO_4^{2-}\quad(Z_AZ_B=+2)$$

$$Co(OC_2H_5)N{:}NO_2^-+OH^-=N_2O+CO_3^{2-}+C_2H_5OH\;(Z_AZ_B=+1)$$

then k will increase with ionic strength.

Finally, if Z_AZ_B is negative, as for the reactions

$$H_2O_2+2H^++2Br^-=2H_2O+Br_2\;(Z_AZ_B=-1)$$

$$[Co(NH_3)_5\,Br]^{2+}+OH^-=[Co(NH_3)_5(OH)]^{2+}+Br^-\quad(Z_AZ_B=-2)$$

k will decrease with increasing ionic strength.

It should be borne in mind that equation (17.93) holds with high accuracy for a number of reactions only in dilute solutions. In concentrated solutions where the Debye-Huckel equation breaks down, some deviations have been observed, and these deviations can be explained in terms of formation of ion-pairs.

17.18. KINETICS IN CHEMICAL ENGINEERING

The work of the chemical engineer involves scaling up processes that have been tested in a laboratory scale so they can be carried out in industrial sized plant. One type of reactor used for carrying out reactions in chemical factories is the continuous flow reactor. In these, the reactants are fed in continuously, stirred within the reactor and products and unchanged reactants continually run out. It generally pays to allow less than full conversion of reactants into products because after a certain percentage conversion, in additional time, the material is held within the reactor and is not compensated for by the better yield. Consider a first order reaction of the type

$$A\rightarrow\text{Products}$$

A will be fed into a continuous reactor in which perfect mixing occurs. If the valume of the reactor is V dm^3 and the volumetric flow rate is udm^3 min^{-1}, then the mean retention time, t, of the material in the reactor is :

$$t=\frac{V}{u}$$

For an initial concentration $[A]_o$ of A entering the reactor, the moles of A entering in time t is $[A]_o\,ut$.

Similarly if $[A]$ is the concentration of A leaving the reactor, the moles of A existing in time t is $[A]\,ut$. That is

$$\text{moles reacting in time } t=\text{rate}\times Vt=k[A]Vt$$

or

moles entering the reactor = moles leaving the reactor + moles which have reacted

$$[A]_oUt=[A]Ut+k[A]Vt$$

Dividing by Ut we get,

$$[A]_o=[A]+k[A]\,\frac{V}{U}$$

This rearranges to

$$\frac{V}{U}=\frac{[A]_o-[A]}{k[A]}=t$$

This design equation can be used to calculate the efficiency of conversion of A into products within a reactor of known volume under a variety of conditions of volumetric flow rate, thus allowing the optimum conditions to be deduced.

PROBLEMS

1. What do you understand by the term order of a reaction? Derive an expression for the first and second order reaction.

2. A first order reaction is 40 per cent complete at the end of 50 min. What is the value of the rate constant in sec^{-1}? In how many minutes, will the reaction be 80 per eent complete?

Ans. 1.7×10^{-4} sec^{-1}; 157.8 min

3. (*a*) Give a brief account of the methods for determining the order of reaction.

(*b*) Optical rotation of sucrose in 1 N HCl at various times was given as below:

Time (minutes)	0	7.8	18.00	27.05	∞
Rotation (degree)	+24.09	+21.7	+17.7	+15	−10.74

(*i*) Show that inversion of sucrose is a first order reaction.

(*ii*) When is the solution optically inactive?

Ans. 109 minutes

4. (*a*) What is meant by half-life period? Derive the equation for the calculation of half-life period.

(*b*) Calculate the order of the reaction from the following data:

$$2NH_3 \xrightarrow{\text{Catalyst}} N_2 \quad +3H_2$$

Pressure (mm Hg)	50	100	200
Relative half-life period	3.52	1.82	0.93

5. (*a*) The order of a reaction is an experimentally determined quantity, explain.

(*b*) For the chemical reaction

$$5Br^-+BrO_3^-+6H^+=3Br_2+3H_2O$$

the rate expression is given as

$$\text{Rate}=k[Br^-]\,[BrO_3^-]\,[H^+]^2.$$

What is the molecularity and order of each reactant?

Ans.

Reactant	Order	Molecularity
Br^-	1	5
BrO_3^-	1	1
H^+	2	6

6. The inversion of sucrose in the presence of HCl gave the following values for the optical rotations:

Time (minutes)	0	15	30	45	63	∞
Optical rotation (degrees)	+32.4	+28.8	+25.5	+22.4	+19.6	−11.0

Show that the inversion of sucrose is a first order reaction.

7. If a chemical reaction proceeds in a sequence of steps then the slowest step is the rate controlling step. Explain the statement.

8. The rate expression for the chemical reaction $A_2+B=C$ is $Rate=k[A_2]$ What is a possible mechanism for this reaction?

9. The following mechanism has been proposed for a chemical reaction:

$$(CH_3)_3CCl=CH_3)_3C^{+}+Cl^{-} \text{slow}$$

$$(CH_3)_3C^{+}+OH^{-}=(CH_3)_3COH \text{ fast}$$

Write the rate expression and the overall reaction.

Ans. $Rate=k[CCH_3)_3CCl]$

$$(CH_3)_3CCl+OH^{-}=(CH_3)_3COH+Cl^{-}$$

10. What is meant by a 'zero-order-reaction'? Deduce a relationship between concentration and time for a given fractional change.

11. From the following data, show that the decomposition of H_2O_2 in aqueous solution is monomolecular,

Time (in minutes)	0	10	20
N	22.8	13.8	8.25

where N is the number of c.c. of $KMNO_4$ required to decompose a definite volume of H_2O_2.

12. *A* gram mole of ethyl acetate was hydrolysed with gm. mole of NaOH. The concentration of the alkali fell according to the following data:

Time (min.)	0	4	6	10	14	20
$(a-x)$	8.04	5.30	4.58	3.50	2.70	2.22

Show that the reaction is bimolecular.

13. For the chemical reaction $A+2B=C$,

it has been found that the rate of the reaction increased by a factor of 2.82 when the concentration of *A* was doubled and increased by 9 when the concentration of *B* was tripled. What is the rate expression; the order of each component and the order of reaction?

Ans. Reaction order=3.5

14. Explain with the help of examples, bimolecular, unimolecular and pseudomolecular reactions?

15. The reaction

$$2O_3=3O_2$$

was found to obey the experimental law

$$-d[O_3]/dt=K[O_3]^2/[O_2]$$

Suggest a mechanism for this reaction.

16. Explain the term energy of activation. How is the energy of activation of a reaction determined?

17. Explain the following:

(*a*) The rate constants for third order reactions are less than those for second order reactions.

(*b*) The velocity of the molecules increases with the increase of temperature.

(*c*) As the velocity of the molecules increases, the number of collisions which a molecule makes per second also increases.

18. The reaction of hexaquochromium ion (III) and thiocyanate ion to form a complex ion

$$Cr(OH_2)_6^{+3}+SCN^{-}=Cr(OH_2)_5NCS^{+2}+H_2O$$

is governed by the rate law

$$\text{Rate}=k[Cr(OH_2)_6^{+3}]\,[SCN^-]$$

The value of k is 2.00×10^{-6} litre/mole-sec. at 14°C and 2.2×10^{-5} litre/mole-sec. at 30°C. What is the value of E_a? (R=1 99 cal/mole-deg)

Ans. 26 Kcal/mole

19. Give an account of collision theory of reaction rates. How would you account for (*a*) mono-molecular reactions, and (*b*) bimolecular reactions using this theory.

20. Explain what is meant by (*a*) consecutive reactions, (*b*) chain reactions and (*c*) side reactions.

21. Write notes on the following:

(*a*) Third order reaction

(*b*) Absolute theory of reaction rates

(*c*) Complex reactions

(*d*) Partition function

(*e*) Primary salt effect.

Chapter 18

CATALYSIS

13.1. INTRODUCTION

A catalyst is a substance which alters the speed of a chemical reaction without undergoing any chemical change and can be recovered at the end of the reaction. The phenomenon of acceleration or retardation of the speed of a chemical reaction by the addition of small amounts of foreign substances to the reactants is referred to as catalysis.

Consider, for example, the decomposition of potassium chlorate. This reaction takes place very rapidly and at a low temperature if a pinch of manganese dioxide is added.

$$2KClO_3 \xrightarrow{MnO_2} 2KCl+3O_2$$

Manganese dioxide does not undergo any chemical change at the end of the reaction and can be recovered and used over again. Thus manganese dioxide acts as a catalyst.

There are numerous examples of catalyzed reactions. Some common examples are:

(*i*) Oxidation of sulphur dioxide to sulphur trioxide in the presence of platinum as a catalyst.

$$2SO_2+O_2 \xrightarrow{Pt} 2SO_3$$

(*ii*) Combination of hydrogen and oxygen in the presence of platinum.

$$2H_2+O_2 \xrightarrow{Pt} 2H_2O$$

(*iii*) In the manufacture of ammonia by Haber's process, iron acts as a catalyst.

$$N_2+3H_2 \xrightarrow{Fe} 2NH_3$$

(*iv*) Hydrogenation of unsaturated hydrocarbons in the presence of nickel.

$$-CH{=}CH-+H_2 \xrightarrow{Ni} -CH_2-CH_2-$$

18.2. GENERAL CHARACTERISTICS OF CATALYZED REACTIONS

Although there are various types of catalyzed reactions, but in spite of their many differences, they show the following characteristic properties:

(*i*) **The catalyst remains unchanged in chemical composition at the end of the reaction**. The amount of the catalyst recovered at the end of the reaction is found to be the same as the amount taken at the start of the reaction. Hence, a catalyst does not undergo any chemical change although its physical form may change completely. Thus manganese dioxide, used as a catalyst in the decomposition of potassium chlorate, changes from coarsely powdered form to fine powder at the end of the reaction. Similarly, a smooth platinum gauze, used as a catalyst in the oxidation of ammonia, becomes rough after some time.

(*ii*) **Only a small amount of the catalyst is required to bring about a reaction**. There are many cases known where a very small amount of the catalyst is sufficient to convert large quantities of the reactants into the products *e.g.*, one gram of platinum is sufficient to cause decomposition of 10^8 litre of hydrogen peroxide.

This is not invariably true. There are some homogenous catalyzed reactions where the rate of the reaction increases with the increase in the concentration of the catalyst as, for example, the inversion of cane sugar in presence of hydrochloric acid which acts as a catalyst. There are also some heterogenous reactions where the rate proportionally increases with the increase in the area of the surface of the catalyst.

Attempts have been made to determine the exact quantity of the catalyst required for a reaction, but it has not been very successful.

(*iii*) **A catalyst does not alter the final position of equilibrium in a reversible reaction and hence does not modify the value of the equilibrium constant**. It has been found from thermodynamics that whether a reversible reaction takes place in the presence of a catalyst or not, the free energy of the process is same. A catalyst accelerates equally the rates of both forward and reversible reactions and helps to establish equilibrium quickly.

This has been found to be true where the amount of the catalyst used is small. If the catalyst is present in large quantity, the magnitude of the equilibrium constant changes. For example, in the hydrolysis of ethyl acetate in presence of large quantity of the catalyst, HCl, the equilibrium constant is affected.

(*iv*) **A catalyst does not start or initiate a reaction, but it merely increases or decreases its speed**. A catalyst simply changes the speed of a reaction which is already proceeding, though very slowly. The function of the catalyst is to help a reaction to attain an alternative path which requires minimum energy of activation.

(*v*) **A catalyst is specific in action.** This implies that a given catalyst can catalyze only a particular reaction and cannot be used to bring about every reaction. For example, manganese dioxide will catalyze only decomposition of potassium chlorate and will fail to catalyze other reactions. Similarly, enzymes are also specific in action.

Thus a proper catalyst for a particular reaction is chosen after numerous experiments.

(*vi*) **A catalyst has an optimum temperature**—the temperature at which the catalyst is most active.

(*vii*) **A catalyst is poisoned by the presence of small quantities of certain substances called catalytic poisons.** Some of the most powerful catalytic posions are arsenious oxide, hydrogen cyanide and carbon monoxide. The presence of these substances makes the catalyst inactive.

(*viii*) **The activity of a catalyst is enhanced by the presence of a substance called Promoter.** For example, in Haber's process for the manufacture of ammonia, molybdenum is used as a promoter to the catalyst iron.

18.3. TYPES OF CATALYSIS

There are generally two types of catalysis : (*i*) Homogeneous catalysis, and (*ii*) Heterogeneous catalysis.

(*i*) **Homogeneous catalysis.** In this type, the catalyst is present in the same phase as the reactants. There can be gaseous or liquid phase.

Examples of homogeneous catalysis in gas phase. Catalyzed homogeneous gas reactions are very rare. A common example of this is the oxidation of sulphur dioxide to sulphur trioxide in the presence of nitric oxide in the lead-chamber process of sulphuric acid.

$$2SO_2+O_2 \xrightarrow{NO} 2SO_3$$

Nitric oxide can also catalyze the combination of carbon monoxide and oxygen and the decomposition of nitrous oxide to nitrogen and oxygen.

$$2CO+O_2 \xrightarrow{NO} 2CO_2$$

$$2N_2O \xrightarrow{NO} 2N_2+O_2$$

Another example is the decomposition of methyl-ethyl, diethyl and di-isopropyl ethers in the presence of iodine vapors which acts as a catalyst.

Iodine vapors also act as a catalyst in the decomposition of acetaldehyde.

$$CH_3CHO \xrightarrow{I_2\text{ vapors}} CH_4+CO$$

If is found to be of second order and the rate is given by

$$\frac{dx}{dt}=kC_{CH_3CHO.}\ C_{I_2}$$

To account for this, it is said that the reaction takes place in two steps:

(1) $CH_3CHO+I_2 \longrightarrow CH_3I+HI+CO$

(2) $CH_3I+HI \longrightarrow CH_4+I_2$

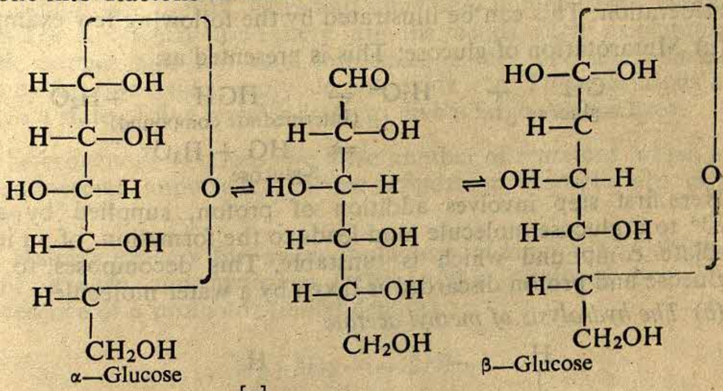
The first reaction being slower determines the rate of the reaction.

Examples of homogeneous catalysis in liquid phase. There are many examples of homogeneously catalyzed reactions in solution. The most common are catalyzed by hydrogen or hydroxyl ions and are generally included under the heading of *acid-base catalysis.* Hydrogen ions are found to catalyze reactions such as the inversion of sucrose and hydrolysis of esters. For such reactions, the rate is proportional to the concentration of hydrogen ions and the concentration of the subtrate *i.e.*, reacting molecule or ion.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}}+H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6}+\underset{\text{Fructose}}{C_6H_{12}O_6}$$

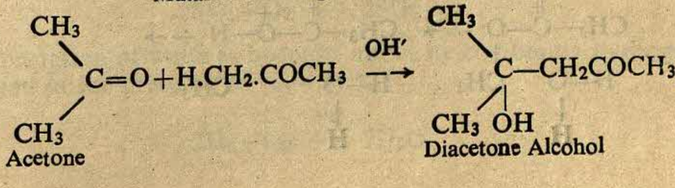
$$\underset{\text{Ethyl Acetate}}{CH_3COOC_2H_5}+H_2O \xrightarrow{H^+} CH_3COOH+C_2H_5OH$$

Similarly, hydroxyl ions are found to have catalytic effect for reactions such as the mutarotation of glucose and the conversion of acetone into diactone alcohol.



$[\alpha]_D=+110°$ $[\alpha]_D=+52.5°$ $[\alpha]_D=+19.7°$

Mutarotation of glucose by OH′



These days, it has been observed that for many reactions which are catalyzed by hydrogen ions, any other substance which is an acid in the Bronsted sense (proton donor) can act as a catalyst for the reaction. This is called *general acid catalysis*. Similarly *general base catalysis* refers to reactions which are catalyzed by all bases (proton acceptor).

There are some reactions *e.g.*, the mutarotation of glucose and the enolization of acetone which are catalyzed by both acids and bases and are known as *general acid-base catalysis*.

For such reactions, the general expression for the measured specific rate constant (K) for the overall reaction may be written as:

$$K = K_0 + \sum K_{acid}\, C_{acid} + \sum K_{base}\, C_{base}$$

where K_0 is the rate constant for the non-catalyzed reaction such as occurs in neutral solution and K_{acid} and K_{base} are the catalytic co-efficients for each species of acid and base (in accordance with the Lowry's concept of acid and base) of concentrations C_{acid} and C_{base} respectively. The value of K_{acid} can be measured from solutions which are strongly acidic (C_{base} is extremely small) and that of K_{base} from solutions which are strongly basic (C_{acid} is small). By knowing K_{acid} and K_{base}, one can easily compare the catalytic effects of various acids and bases).

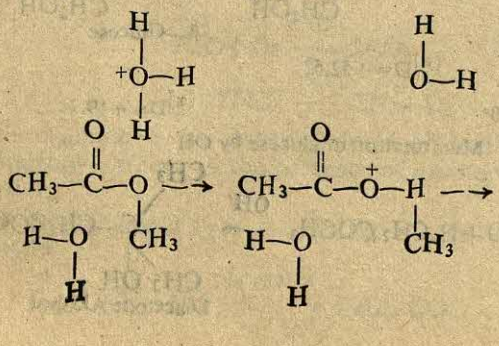
In considering the mechanism of acid or base catalyzed reactions, addition, or removal of a proton by a catalyst must be taken into consideration. This can be illustrated by the following few examples:

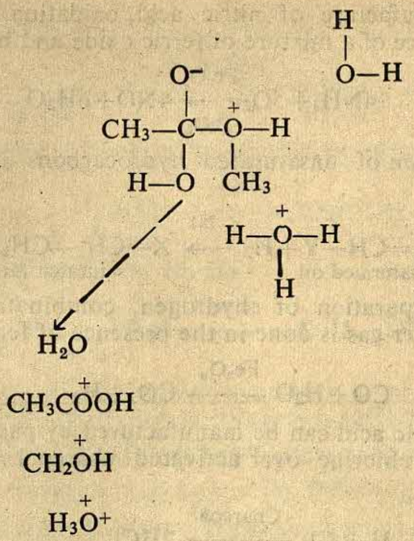
(*a*) Mutarotation of glucose: This is presented as:

$$\underset{\text{L-gluccse}}{GH} + H_3O^+ \rightleftharpoons \underset{\text{(Intermediate compound)}}{HGH} + H_2O$$
$$\rightleftharpoons \underset{\beta\text{-glucose}}{HG} + H_3O^+$$

Here first step involves addition of proton, supplied by acid, H_3O^+ to a glucose molecule and leads to the formation of an intermediate compound which is unstable. This decomposes to give β-glucose and proton discarded is taken by a water molecule.

(*b*) *The hydrolysis of methyl acetate*





It is clear that for such reactions water acts both as an acid and a base as it supplies as well as accepts a proton.

(*ii*) **Heterogeneous catalysis.** In this type, catalyst constitutes a separate phase from the reactions. The catalyst is generally solid and reactants are mostly gases and sometimes liquids. The catalysts which are frequently used here are the metals such as platinum, nickel, copper and iron and sometimes oxides of metals such as ferric oxide, zinc oxide, molybdenum oxide etc. These catalysts are used in a state of fine powder so as to give a large surface area.

In heterogenous catalysis, we have number of reactions which are of commercial importance. Some important example are given below:

(*i*) Haber's Process for the manufacture of ammonia : Combination of nitrogen and hydrogen (ratio 1 : 3) is catalyzed by iron in the presence of a promotor (molybdenum).

$$N_2+3H_2 \xrightarrow{Fe} 2NH_3$$

(*ii*) Contact process for the manufacture of sulphuric acid. Combination of sulphur dioxide and oxygen in the presence of platinum.

$$2SO_2+O_2 \xrightarrow{Pt} 2SO_3$$

(*iii*) Formation of water is brought about by combining hydrogen and oxygen in the presence of platinum.

$$2H_2+O_2 \xrightarrow{Pt} 2H_2O$$

(*iv*) In the manufacture of nitric acid, oxidation of ammonia is done in the presence of a mixture of ferric oxide and bismuth oxide.

$$4NH_3+5O_2 \xrightarrow[BiO_2]{Fe_2O_3} 4NO+6H_2O$$

(*v*) Hydrogenation of unsaturated hydrocarbons in the presence of nickel.

$$\underset{\text{Unsaturated oil}}{X-CH=CH-Y+H_2} \xrightarrow{Ni} \underset{\text{saturated fat}}{X-CH_2-CH_2-Y}$$

(*vi*) In the preparation of hydrogen, combination of carbon monoxide and water gas is done in the presence of ferric oxide.

$$CO+H_2O \xrightarrow{Fe_2O_3} CO_2+H_2$$

(*vii*) Hydrochloric acid can be manufactured by passing a mixture of hydrogen and chlorine over activated charcoal prepared from woods.

$$H_2+Cl_2 \xrightarrow{\text{Charcoal}} 2HCl$$

18.4. ENZYME CATALYSIS

This is an important type of catalysis and comprises the chemical reactions in living organisms which are catalyzed by enzymes. The enzymes are complex organic compounds (proteins) of very high molecular weights and are not very stable. Since the particle diameter of each enzyme is in the range of 100 to 1000A, therefore, they form colloidal solutions with water and hence enzyme catalysis lies in between the homogeneous and heterogeneous catalysis and is sometimes referred to as microheterogeneous. The catalytic action of each enzyme is extremely specific in nature. For reversible reactions, enzymes like other catalysts, catalyze equally both the forward and reverse reactions without disturbing the equilibrium.

There are numerous reactions known which are catalyzed by enzymes. Majority of the reactions are connected with the natural processes. Some important examples are:

(*i*) Hydrolysis of starch by means of diastase obtained from germinating barley

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n}+nH_2O \xrightarrow{\text{Diastase}} \underset{\substack{\text{Maltose}\\\text{sugar}}}{nC_{12}H_{22}O_{11}}$$

(*ii*) Hydrolysis of maltose into glucose by maltase

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}}+H_2O \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

(*iii*) Conversion of sucrose into a mixture of glucose and fructose by invertase.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}}+H_2O \xrightarrow{\text{Invertase}} \underset{\text{glacose}}{C_6H_{12}O_6}+\underset{\text{fructose}}{C_6H_{12}O_6}$$

(*iv*) Conversion of glucose into alcohol by zymase

$$\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} 2C_2H_5OH+2CO_2$$

(*v*) Hydrolysis of urea by urease

$$\underset{\text{Urea}}{NH_2CONH_2}+H_2O \xrightarrow{\text{Urease}} 2NH_3+CO_2$$

Amount of urease required for hydrolysis is very small. Only one part of enzyme in ten million of solution is sufficient.

(*vii*) Hydrolysis of peptide glycyl-L-glutamyl-L-tyrosine by pepsine.

All enzymes belong to any one of the following two classes:

(*a*) *The hydrolytic enzymes* These are complex acid-base catalysts and accelerate ionic reactions, mainly the transfer of hydrogen ions, and

(*b*) *The oxidation-reduction enzymes.* These enzymes catalyze electron transfers.

Mechanisation of enzyme reaction. The detailed mechanism of the enzyme action has not been exactly determined so far. The simplest mechanism of the enzyme reaction, originally suggested by Michaelies and Menten, is represented by the following reaction scheme:

$$E+S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\text{complex}}{ES} \xrightarrow{k_3} E+P \qquad \ldots (18.1)$$

where *E* represents the enzyme, *S* the reactant generally known as substrate in the enzyme-catalyzed reaction, *ES* the intermediate complex between the enzyme and substrate and *P* is the reaction product.

k_1, k_2 and k_3 are the rate constants for the various reactions. The rate equations are:

$$\frac{-d[S]}{dt}=\frac{d[P]}{dt}=k_1[E][S]-k_2[ES]=k_3[ES] \qquad \ldots (18.2)$$

and

$$\frac{d[ES]}{dt}=k_1[E][S]-k_2[ES]-k_3[ES] \qquad \ldots (18.3)$$

All the terms in the bracket represent the various concentration terms.

Equation (8.2) gives the formation of the product or disappearance of the substrate and equation (18.3) gives the formation of the complex.

Since the molar concentration of the enzyme is very small as compared to the molar concentration of the substrate, therefore, we can write the conservative equation

$$[E]_0=[E]+[ES] \qquad \ldots (18.4)$$

where $[E]_0$ is the initial concentration of the enzyme.

Putting $[E]=[E]_0-[ES]$ in equation (18.3),

$$\frac{d[ES]}{dt}=(k_1[E]_0-[ES])[S]-k_2[ES]-k_3[ES]$$

$$=k_1\,[E]_0\,[S]-(k_1[S]+k_2+k_3)[ES] \qquad \ldots (18.5)$$

Under steady-state,

$$\frac{d[ES]}{dt}=0$$

Therefore,

$$0=k_1[E]_0\,[S]-(k_1[S]+k_2+k_3)\,[ES]$$

or

$$[ES]=\frac{k_1\,[E]_0\,[S]}{k_1[S]+k_2+k_3} \qquad \ldots (18.6)$$

Dividing the numerator and denominator of the right hand side of equation (18.6) by k_1 $[S]$; we get

$$[ES]=\frac{[E]_0}{1+\dfrac{k_2+k_3}{k_1[S]}} \qquad \ldots (18.7)$$

Substituting this value of $[ES]$ in equation (18.2) which gives the formation of the product *i.e.*, equation $\frac{d[P]}{dt}=k_3\,[ES]$, we get

$$\frac{d[P]}{dt}=\frac{k_3[E]_0}{1+\dfrac{k_2+k_3}{k_1[S]}} \qquad \ldots (18.8)$$

The quantity $\frac{k_2+k_3}{k_1}$ is called the *Michaelies Constant* and becomes equal to the concentration of substrate, $[S]$ if the rate of formation of the product is half the maximum rate of the reaction.

Equation (18.8) is in agreement with the experimental fact that for *very low concentration of S*, every enzyme catalyzed reaction is found to be of first order and the rate is proportional to the concentration of S. If the *concentration of S is very high*, the rate becomes of zero order and is independent of the concentration. But in *both the cases, the reaction is of first order with respect to the initial concentration of the enzyme.*

18.5. THEORIES OF CATALYSIS

There are many different kinds of catalysts and many different mechanisms by which catalysts operate have been proposed. In homogeneous catalysis, the catalyst is a molecule or ion in homogeneous solution and in heterogeneous catalysis, the reaction occurs on the surface of the solid catalyst.

The action of a catalyst can be explained as follows:

Let us consider a reaction

$$\text{Reactants} \rightleftharpoons \text{Products}$$

In order to carry out the above reaction, the reactants have to be activated so that they acquire the energy E_a, the energy of activation of the uncatalyzed reaction, indicated by the thick curve in the diagram. When a catalyst is added, the height of the energy barrier is lowered and more and more reactant molecules can now cross the new energy barrier-E, indicated by the dotted curve and thus increase the rate of the reaction.

It is not possible to give a uniform explanation of the mechanism of the catalytic reactions. The two more important mechanisms have been proposed: (1) Intermediate compound formation theory and (2) Adsorption theory.

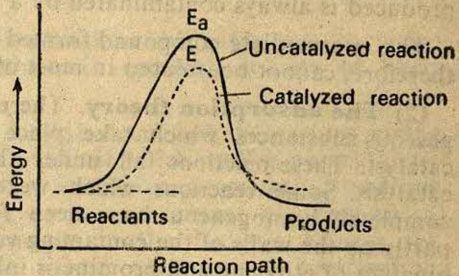


Fig. 18-1. Energy of activation for the uncatalyzed and catalyzed reaction.

(1) **Intermediate compound formation theory**. According to this theory, a catalyst must enter into chemical combination with one or more of the reactants forming an intermediate compound or substrate (catalyst complex) which then decomposes or combines with one of the reactants to form the product and the catalyst is regenerated. Let us consider a reaction involving the combination of the reactants A and B to give the product AB, *viz.*,

$$A+B=AB \text{ (uncatalyzed reaction)}$$

The reaction will be very slow in the absence of a catalyst. On the addition of a small amount of catalyst C, the reaction will proceed along the following stages:

$$A+C=AC^* \quad \text{(Intermediate compound)}$$
$$AC^*+B=AB+C$$

The intermediate compound AC^* helps the reaction to proceed in stages with low energy of activation thereby accelerating the rate of a chemical reaction.

The role played by the copper catalyst in the formation of water from the combination of hydrogen and oxygen can be symbolised in the form of following equations:

$$2Cu+\tfrac{1}{2}O_2 \rightarrow Cu_2O \text{ (Intermediate compound)}$$
$$Cu_2O+H_2 \rightarrow 2Cu+H_2O$$

The preparation of oxygen by heating a mixture of manganese dioxide and potassium chlorate is another example where intermediate compound formation has been suggested according to the following sequences of reactions; manganese dioxide acts as a catalyst.

$$2MnO_2+2KClO_3=2KMnO_4+Cl_2+O_2$$

$$2KMnO_4=K_2MnO_4+MnO_2+O_2$$

$$K_2MnO_4+Cl_2=2KCl+MnO_2+O_2$$

The above mechanism is supported by the fact that oxygen thus produced is always contaminated by a small quantity of chlorine.

The intermediate compound formed has a very low stability and therefore, cannot be isolated in most of the cases.

(2) **The adsorption theory.** There are many reactions between gaseous substances which take place in the presence of a solid catalyst. These reactions fall under the category of heterogeneous catalysis. Some reactions which were at one time thought to be completely homogeneous have been found to take place at least partly on the walls of the containing vessel. For example, the combination of ethylene and bromine is inhibited if the interior of the glass reaction vessel is coated with paraffin. On the other hand, if the vessal is coated with stearic acid, the reaction occurs more rapidly. It has been suggested by Langmuir in 1916 that the catalytic action of a surface depends on its adsorption of the reactants. The molecules of the reacting gases are adsorbed at different points on the surface of a catalyst. These adsorbed molecules may then combine to form an adsorbed activated complex which then decomposes to form the products which are desorbed from the surface. A surface reaction can usually be broken into following steps:

(*i*) Diffusion of reactants to surface.

(*ii*) Adsorption of reactants at surface.

(*iii*) Chemical reaction on the surface.

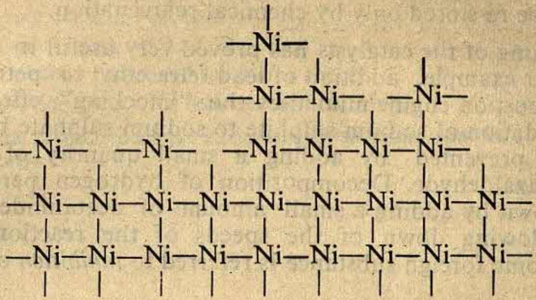
(*iv*) Desorption of products from the surface.

(*v*) Diffusion of products away from the surface

The rate determining step is usually the step (*iii*) which is the slowest step.

It has been observed that chemisorption plays an important role in the surface catalysis. The stronger forces are operative in chemisorption which tend to bring about a partial loosening of the bonds in the adsorbed reacting molecules and a very small energy is required to form the activated complex for the reaction.

It has been found that there are some active centres on the surface of a catalysts where the adsorption takes place. X-ray studies of catalysts show that there are unsatisfied forces present on the surface of a catalyst, which can be used to attach molecules. The surface of a nickel catalyst may be represented as follows:



Isolated nickel atoms and discontinuities probably act as active centres. This explains the enhanced catalytic activity of finely divided catalysts.

Promoters. The activity of a catalyst can be enhanced by mixing it with a small quantity of a material which itself is non-catalytic or a feeble catalyst. This substance is called a *promoter*. Numerous examples of promoter action are known and several of them are of industrial importance. For example in the Haber's Process for the synthesis of ammonia, the mixed catalysts of composition $Fe+Al_2O_3+K_2O$ are very aclive. The small amounts of aluminium and potassium oxides promote the activity of the catalyst iron.

The promoter action can be explained by suggesting that the promoter increases the number of active centres of the catalytic surface.

18.6. CATALYTIC POISONING

There are certain substances which, if present even in small quantities, are sufficient to diminish the rate of the reactions. These substances make the catalyst useless and are termed *catalytic poisons*. For example, in the manufacture of sulphuric acid by contact process, activity of the platinum catalyst is very much reduced if some arsenious oxide is present as impurity in sulphur dioxide and oxygen. The decomposition of hydrogen peroxide by colloidal platinum is paralysed by hydrocyanic acid. The activity of iron catalyst in the manufacture of ammonia by Haber' process is reduced if nitrogen and hydrogen gases are contaminated with carbon monoxide.

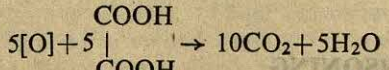
The reason for the poisoning of catalysts in probably due to the preferential adsorption of the poison on the active centres of the catalyst. This renders the catalyst useless. The poisoning of the catalyst may be temporary or permanent. If the poison is held on the surface of the catalyst by physical forces, the poisoning is temporary and can be removed by removing the poisons. But, if the poison is held on the surface of the catalyst by strong chemical forces, the poisoning is permanent. In such cases, activity of the catalyst can be re-stored only by chemical rejuvenation.

The poisoning of the catalysts has proved very useful in many of the cases. For example, addition of lead tetra ethyl to petrol in an internal combustion engine minimises the "knocking" effect. Similarly, the oxidation of sodium sulphite to sodium sulphate by oxygen gas can be prevented by adding a small quantity of alcohol, aniline or benzaldehyde. Decomposition of hydrogen peroxide can be slowed down by adding a small amount of acetanilide or glycerine. The slowing down of the speeds of the reactions by the addition of some foreign substance is referred to *inhibition* or *negative catalysis*.

18.7. AUTOCATALYSIS

There are certain reactions in which one of the products formed during the course of the reaction catalyze the reaction. For example, in the titration of oxalic acid by potassium permanganate, it has been observed that when first portion of permanganate is added to hot oxalic acid, the reaction is slow and it takes some time for the decolorisation of permanganate. However, the second portion and succeeding portions of permanganate are decolorised quickly. This is due to the presence of manganous ions formed dnring the course of the reaction.

$$2KMnO_4+3H_2SO_4 \rightarrow K_2SO_4+2MnSO_4+3H_2O+5[O]$$



$$5[O]+5\begin{array}{c}COOH\\|\\COOH\end{array} \rightarrow 10CO_2+5H_2O$$

Similarly, in the action of nitric acid on copper, the reaction is slow in the beginning but becomes fast as soon as nitrous acid is formed during the course of the reaction.

This phenomenon in which one of the products of the reaction itself acts as a catalyst is known as *auto-catalysis*.

PROBLEMS

1. What are the characteristics of a catalyst? Discuss the influence of catalysis on chemical reactions.

2. Discuss the mechanism of homogeneous catalysis giving suitable examples.

3. Discuss the catalytic role of acids and bases in the mutarotation of glucose.

4. Give a brief account of heterogeneous catalysis with special reference to its applications to chemical industry.

5. Explain giving examples of the following terms:

(*a*) Catalytic poisons

(*b*) Action of promoters

(*c*) Active centres

(*d*) Auto-catalysis

(*e*) The specific nature of catalyst.

6. Write short notes on the following:

(*a*) Intermediate compound formation theory

(*b*) Adsorption theory for heterogeneous catalysis.

7. In what respects does the enzyme catalysis differ from and resemble heterogeneous catalysis?

Chapter 19

COLLOIDS

19.1. INTRODUCTION

A solution consists of two components—a solute and a solvent. If a solution of ferric chloride is poured into boiling water, a clear deep brown liquid is obtained. The change in colour shows that a chemical reaction has occurred; in fact ferric oxide has been formed. The latter is practically insoluble in water and would normally precipitate but if formed under the right conditions, it may remain dispersed throughout the liquid in the form of very small particles. The presence of these particles is shown by the colour but they are not large enough to cause the liquid to appear cloudy. This is an example of a colloidal system. In ordinary true solution, the solute is dispersed throughout the solvent in the form of single molecules or ions. On the other hand, a suspension contains particles that are large enough to be seen by the naked eye or through the microscope. Colloids occupy an intermediate position between true solutions on one hand and suspensions on the other.

The word colloids is of Greek origin; the Greek word Kolla, meaning "glue". Thomas Grahm is usually regarded as the founder of Colloid Science.

It is obviously impossible to draw a boundary line between true solutions and colloidal solutions. Colloidal behaviour can be connected with greatly increased surface area compared with the volume as the size is reduced. The essential properties of colloidal dispersions can be ascribed to the fact that the ratio of surface area to volume of the particles is very large. In the true solution, the system consists of one phase only and there is no true surface of separation between the molecular particles of solute and solvent. The size of particles in Colloidal state ranges between 5 $m\mu$—200 $m\mu$. Ostwald regarded colloidal systems as heterogeneous in character, consisting of two phases: (*i*) Disperse phase and (*ii*) Dispersion medium.

Disperse phase refers to the phase forming the particles.

Dispersion medium is the medium in which dispersion of the particles takes place.

The colloidal dispersions are thermodynamically unstable and tend to coagulate and precipitate on standing unless suitable precautions are taken. Since both the disperse phase and dispersion medium may be solid, liquid or gaseous, there can be several different types of colloidal system. No example of colloidal dispersion of one gas in another gas is known. Various types of colloidal dispersions known are given in Table 19.1.

TABLE 19.1.

Types of colloidal dispersions

Dispersion medium	*Disperse Phase*	*Name*	*Examples*
Gas	Gas	—	Unknown
	Liquid	Aerosol	Fogs, mists, clouds
	Solid	Aerosol	Smokes
Liquid	Gas	Foam	Whipped cream
	Liquid	Emulsion	Dispersion of water in oil or oil in water
	Solid	Sols	AgCl, Au, As_2S_3 or S, in water
Solid	Gas		Solid foam
	Liquid	Gels	Jellies, minerals with liquid
	Solid	—	Glasses coloured with dispersed metals, ruby, glass

19.2. CLASSIFICATION OF COLLOIDS

Colloidal solutions are known as sols. If the dispersion medium is water, they are called "hydrosols" or sometimes "aquasols." If in a liquid as dispersion medium, the disperse phase is liquid, the colloidal solution is known as emulsion.

Dispersion of solids in liquids can be roughtly divided into two categories lyophobic and lyophilic sols. Lyophobic (solvent hating) sols have little attraction between the disperse phase and dispersion medium. These are relatively less stable as compared with lyophilic sols. On heating or cooling the lyophobic systems, solids are obtained which cannot be reconverted into sols either by adding solvent or by warming. Typical examples of this category of colloids are sols of metals, sulphur and silver halides. Lyophilic (solvent loving) sols on the other hand are systems in which the disperse phase shows some definite affinity for the medium. Lyophilic sols are generally reversible and behave like true solutions to some extent *e.g.*, gums starches and proteins. These substances are absorbed by the disperse phase and are stabilised by strong solvation. Some of the important characteristics of lyophobic and lyophilic sols are listed in Table 19.2.

TABLE 19.2.

Characteristics of lyophobic and a lyophilic colloids

Lyophobic colloids	*Lyophilic colloids*
1. These are generally unstable, get easily coagulated on adding electrolytes.	1 Very stable and are not easily coagulated by electrolytes.
2. Irreversible in character.	2. Reversible.
3. Prepared by indirect methods.	3. Usually prepared by simple solution methods.
4. Viscosity of colloidal dispersion is same as that of the solvent.	4. These are highly viscous systems.
5. These are generally inorganic materials *i.e.* metals, sulphides and oxide sols.	5. Mostly organic materials *e.g.*, starch, proteins, gums etc.
6. Carry electric charge and stability depends on Zeta potential.	6. Carry little or no charge.

19.3. METHODS OF PREPARATION OF COLLOIDAL SOLUTIONS

Certain types of small molecules are capable of associating in solution as a result of their mutual intermolecular interactions to form clusters or aggregates of colloidal dimensions, known as association colloids or micelles. Some important substances which behave in this way are surface active agents, certain dyes (methylene blue) and phospholipids (lecithins). Since solutions of macromolecules and association colloids are true solutions and are thermodynamically stable, they are formed spontaneously on mixing the solute and the solvent, and their preparation presents some problems. Examples include the preparation of aqueous solutions of proteins. dextring starch and the reconstitution of blood serum and plasma. The preparation of concentrated solutions of agar and gelatin requires heating and such solutions form gel on cooling.

There are two ways in which colloidal size particles can be obtained: (*a*) by building up the particles from single molecules. The methods under this category are known as *Condensation* or *Aggregation Methods*, (*b*) by disintegrating down the bulk material to the colloidal particles. Methods under this category are known as the *Dispersion Methods*.

In preparing a colloidal solution, care must be exercised to see that the vessels used should be thoroughly clean and the materials used should be pure.

Condensation methods. A supersaturated solution of the disperse phase is prepared in the dispersion medium by carefully controlling the temperature and keeping the concentration of disperse phase to be low. The various methods used here are:

(*i*) **Reduction method.** It has been used to prepare sols of metals *e g.*, gold, silver and platinum. The method involves the reduction of solutions of their soluble salts or oxides using different reducing agents. The reducing agents employed for the purpose are formaldehyde, hydrogen, carbon monoxide, hydrazine, hydroxylamine, tannin etc. Ostwald prepard colloidal gold solution by reducing gold chloride. A few drops of 0.1 per cent gold chloride solution were added to 100 ml of distilled water. The gold chloride was neutralised with calculated amount of potassium carbonate. A few drops of 0.1 per cent tannin were added and the solution was warmed when a cherry-red gold sol was produced. Tannin has also got some protective action.

(*ii*) **Oxidation method.** Colloidal sulphur may be prepared by the oxidation of hydrogen sulphide. Hydrogen sulphide is passed into a solution of sulphur dioxide in water until all the odour of sulphur dioxide has been removed. Sulphur sol is produced according to the following reaction:

$$2H_2S+SO_2=2H_2O+3S$$

(*iii*) **Ionic equilibria method.** When a solution of silver nitrate is added to a very dilute solution of a chloride, the solution becomes slightly cloudy but no precipitate forms. The reaction can be symbolised as follows:

$$Ag^++Cl^-=AgCl(s)$$

Arsenious sulphide sol is obtained by mixing solutions of hydrogen sulphide and arsenious oxide:

$$2As^{3+}+3S^{2-}=As_2S_3(s)$$

(*iv*) **Hydrolysis method.** This method is used for preparing oxide and hydroxide sols. Ferric oxide sol can be prepared by pouring a solution of ferric chloride into a large volume of boiling water, the reaction being

$$2FeCl_3+6H_2O=Fe_2O_3.3H_2O+6HCl$$

(*v*) **Exchange of solvent method.** In general if a substance *A* is soluble in *B* but insoluble in *C*, the colloidal solution of *A* can be prepared if a solution of *A* and *B* is added to an excess of *C*; the two solvents being miscible with each other.

Sulphur is slightly soluble in alcohol but practically insoluble in water. Sulphur sol can thus be prepared by pouring a saturated solution of sulphur in ethanol into water.

Disperson methods. (*i*) **Bredig's arc method.** This process consists in striking an electric arc between wires of platinum, gold or silver immersed in water as shown in Fig. 19.1. At high temperature, the arc causes the metal to vaporise and the vapors are condensed by water to form colloidal particles. Traces of sodium hydroxide or potassium carbonate are necessary for the stability of the colloidal dispersion. The vessel is cooled in ice. The method was used by Bredig to prepare sols of gold and platinum.

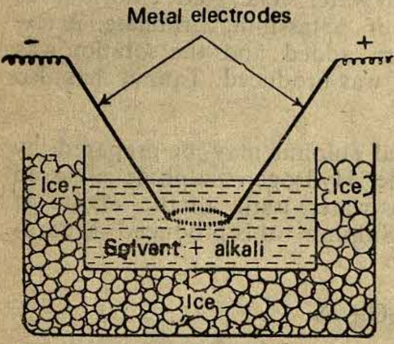


Fig. 19.1. Bredig's arc method.

(*ii*) **Mechanical dispersion method**. This consists in breaking the material down to the colloidal size. The solid and dispersion medium are fed between grinding surfaces, usually concentric cones rotating at a high speed ($\simeq$7,000 revolutions per minute) This device is known as "colloid mills."

(*ii*) **Peptisation method**. It has been found that ionic solids containing a small concentration of a common ion tend to break up spontaneously into colloidal particles. This process is known as peptisation. For example, a precipitate of silver iodide can be peptised by shaking with a dilute solution of either potassium iodide or silver nitrate.

19.4. PURIFICATION OF COLLOIDAL SOLUTIONS

A sol prepared by any one of the above methods very often contains other materials besides the colloidal particles. It is often desirable to remove these impurities, particularly when they are electrolytes as they reduce the stability of the sol.

The methods used for the purification of a colloidal solution are: (*i*) Dialysis, and (*ii*) Ultrafiltration.

(*i*) **Dialysis**. This method makes use of the fact that there is a significant difference in size between colloidal particles and the dissolved molecules or ions. The sol is placed inside a dialyser which consists of a vessel open at both ends. The one end can be covered by a parchment or cellophane membrane. The dialyser is nearly filled with the colloidal solution and suspended in a vessel containing distilled water. Crystalloid gets through and the colloidal particles are retained. The water in the tank is changed periodically or continuously. Graham's dialyser used is shown in Fig. 19.2. The process of dialysis can be quickened by applying an electric field. This process is called *electro-dialysis* and is shown in

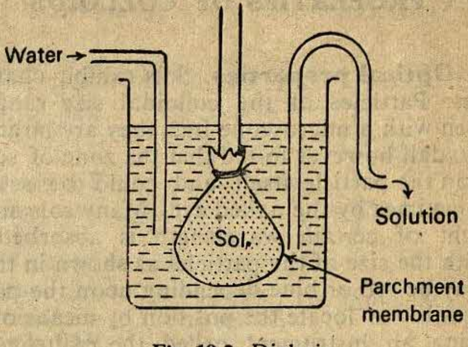


Fig. 19.2. Dialysis.

Fig. 19.3. The colloidal solution along with the unwanted electrolyte is placed between two dialysing membranes and pure water in a compartment on each side. When a high potential is applied, the ions migrate into the water leaving the pure colloidal solution.

The process of dialysis depends essentially on the character of the aggregates involved, the nature of the fluid and the semipermeability of the membrane. The various dialysers which are used are cellulose nitrate and cellulose acetate membranes.

(*ii*) **Ultrafiltration.** This is another important method for purifying sols. The process of ultrafiltration is similar to the filtration of an ordinary precipitate except with the difference that the membrance used here is designed in such a way that it will permit the passage of only electrolytes and medium, and not of colloid particles. Colloid particles thus can be separated in the form of a slime from medium containing electrolytes. Such membranes are made by impregnating ordinary filter paper with collodion or a regenerated cellulose such as cellophon or visking. Other such membranes can be unglazed porcelain and finely sintered glass. Since ultrafiltration membranes are of delicate constitution and can be easily broken, they are generally supported on wire screens particularly when the liquid is being passed through them under pressure. Ultrafiltration being a slow process can be quickened by using pressure or suction.

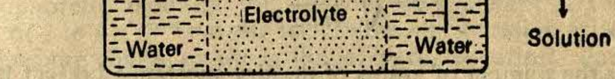


Fig. 19.3. Electro-dialysis.

19.5. PROPERTIES OF COLLOIDS

(*i*) **Optical properties**. Sols exhibit characteristic optical properties. Particles of the colloidal size range are too small to be seen even with a microscope but they are large enough to scatter light. Tyndall however found that the zone of scattered light was larger than the particle itself and could be seen in the microscope or sometimes by the naked eye. Many sols are coloured showing that light of certain wavelength is absorbed. This is also connected with the size of the particles as shown in the case of gold sols which may be red or blue depending upon the particle size. It is, however, possible to locate the position by means of the light that it scatters using an instrument called the "Ultramicroscope" as is shown in Fig. 19.4.

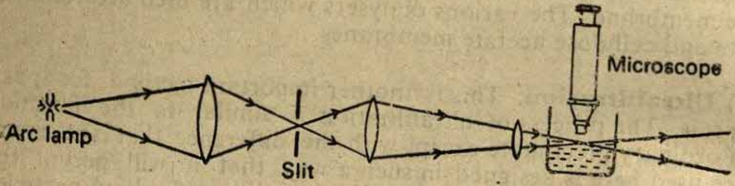


Fig. 19.4. Arrangement of ultramicroscope.

An intense beam of light is passed through the sol and the scattered light is observed through a microscope at right angles to the beam. The number of particles can be counted and it is also possible to decide the shapes of the particles roughly.

Assuming the colloidal particles to be spherical in shape and the density of the substance in the colloidal state to be the same as in the bulk, we can calculate the mean radius r of the particles using the relation

$$r=\sqrt{\frac{3bv}{4\pi n\rho}}$$

where b is the number of grams of the dry substance present per c.c. of the colloidal solution. The number of particles n present in v c.c. of the solution is determined using the ultramicroscope, ρ is the density of the dry substance.

(*ii*) **The Brownian movement**. Robert Brown in 1827 observed that pollen grains executed a ceaseless random motion and travelled a zig-zag path. It has been found that all colloidal particles execute this random zig-zag motion when seen under the ultramicroscope. This motion of the colloidal particles is known as Brownian motion.

Wiener suggested that in colloidal particles, the Brownian motion was arising out of molecular motion. The small colloidal particles are knocked about by collision with the molecules of the dispersion medium.

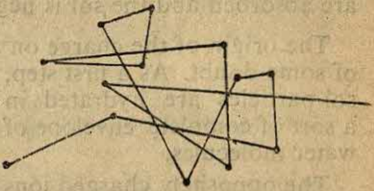


Fig. 19.5. The Brownian movement.

(*iii*) **Electrical properties of colloids**. All sol particles are found to be electrically charged. When a hydrophobic sol is placed in an electric field, the particles move in one direction or another. This slows that the colloidal particles are electrically charged with respect to the dispersion medium. This motion of colloid particles under the action of an electric field is called *electrophoresis*. The potential gradient in volts per cm can be derived from the applied EMF and the dimensions of the apparatus. An electrophoretic apparatus employed for this purpose is shown in Fig. 19.6. It consists of a U-tube of the form shown. It is filled with ferric hydroxide sol, and then distilled water is poured. A high potential is applied between electrodes placed in the water, the boundary between the colloid and the distilled water begins to move towards the cathode. This movement of colloid particles under the action of electric field shows that colloids are charged particles. A large majority of sols are negatively charged; some of the common examples are metals, metallic sulphides, sulphur, clay, cotton, paper and silicic acid. The positive colloids in water consists of a few of the matallic hydroxides and certain dyes.

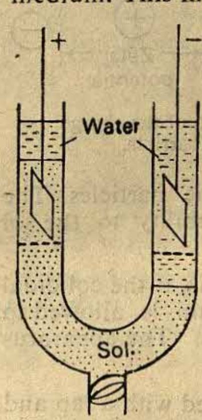


Fig. 19.6. Electrophoretic apparatus.

The velocity of particles under a fall of potential 1 volt per cm is known as the electrophoretic mobility. It has been found that the electrophoretic mobility for aqueous sols always lies within the range of 2 to 4×10^{-4} cm per sec. Now the question arises, in what way does the charge on the colloidal particles arise? Earlier it was thought that the charge was caused by friction, but this has not proved to be the correct explanation. It has been frequently observed that small quantities of electrolytes are necessary for the stability of colloidal systems. They become unstable if the electrolytes are removed by dialysis. It appears, therefore, that traces of ions present in the sol are responsible for both the charge and the stability of the colloidal system. This suggests that the charge is due to the adsorption of ions from solution, the surface of the particles becoming covered with a layer of adsorbed ions. For example in a ferric hydroxide sol if there is an excess of Fe^{3+} ions in the solution, they are adsorbed and produce positively charged particles but if under suitable conditions there are excess of OH^- ions, then these are absorbed and the sol is negative.

The origin of the charge on the colloid particles is still a matter of some doubt. As a first step, sol particles are hydrated in a sort of complete envelope of water molecules.

The oppositely charged ions present in the solution will be attracted by the colloidal particle and an electrical double layer is formed as shown in Fig. 19.7.

This is similar to the one produced when a metal is in contact with a solution of its ions. A potential developed between the surface of the particle and the solution is known as the zeta potential. It is this potential that determines the speed of the particles. The presence of the electrical double layer renders stability to the sol particles.

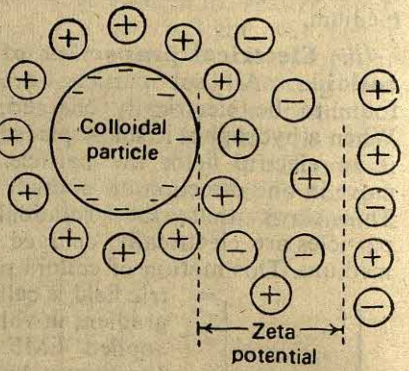


Fig. 19 7. Origin of the charge on the colloidal particle.

Electro-osmosis. In the study of electrophoresis, if the colloidal particles are kept still and only the dispersion medium is allowed to move the phenomenon is known as electro-osmosis. The apparatus used is shown in Fig. 19.8.

It consists of a U-tube having its one limb closed with a tap and provided with a sealed capillary tube *C*. *D* is a porous diaphragm which divides the main compartment into two sections. In each section is placed an electrode as well as portions of the liquid phase.

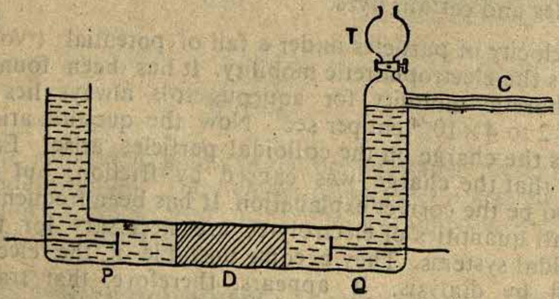


Fig. 19.8. Apparatus used for electro-osmosis.

When an electrical pressure is applied to the electrodes, the solid phase cannot move but the movement of the liquid phase can be observed as the liquid rises in *T*. The rate at which the dispersion medium moves can be measured in terms of the rate of movement of the liquid in capillary *C*.

19.6. PRECIPITATION OF COLLOIDS BY ELECTROLYTES

Numerous terms have been used to denote the process of destroying the colloidal state and causing the dispersed phase to combine in larger aggregates. Precipitation is the most general term which implies, "to separate from a solution." The precipitation of a sol by adding an electrolyte was investigated by Hardy and Schulze. There are two features of the Hardy-Schulze rule, first the ion which is effective in causing precipitation of a sol is the one whose charge is of opposite sign to that of the colloidal particles; the second feature states that the precipitating efficiency increases with the increasing valence of the precipitating ion.

In order to determine the precipitating value of ions, equal volumes of a certain suspension are precipitated by solutions containing the ions under similar conditions of concentration and stirring etc. The precipitating values of some electrolytes on the same colloidal suspension are given in Table 19.3.

There have been several attempts to arrange ions in a series according to their precipitating powers but it is found that such a grouping holds only for the precipitation of a specific sol, and even then a change in physical conditions may upset the series. One such

TABLE 19.3

Equal volumes of the same sol are used with the necessary amount of electrolyte to precipitate

Substance in suspension	*Charge of suspension*	*Electrolyte added*	*Millimoles of electrolyte for precipitation*
As_2S_3	Negative	NaCl	58.0
		KCl	50.0
		$MgSO_4$	0.81
		$CaCl_2$	0.65
		$AlCl_3$	0.093
		$Al(NO_3)_3$	0.095
		$Th(NO_2)_3$	0.090
		NaCl	9.2
		KBr	12.0
		$BaCl_2$	9.6
Fe_2O_3	Positive	K_2SO_4	0.20
		$MgSO_4$	0.22
		$K_2Cr_2O_7$	0.19

series, known as Hofmeister or the lyotropic series, shows the effect of certain anions of neutral salts upon the precipitation of proteins and is given below:

$$SCN^- > I^- > NO_3^- > Br^- > Cl^- > \text{Acetate} > \text{Citrate} > \text{Tartrate} > SO_4^{2-}$$

Sometimes, the precipitation of a colloidal suspension may be done by physical methods, *i.e.*, stirring, shaking, boiling or freezing the sol.

19.7. THE STABILISATION OF THE COLLOIDAL STATE

This process consists in an attempt to neutralise or render ineffective the forces and conditions by which precipitation can be brought about. For example if a stable organic colloid, such as gelatin is added to a metal sol, the latter may be prevented from precipitation on the addition of an electrolyte. The addition of a lyophilic substance to a lyophobic sol usually renders the later less sensitive to the precipitating effect of electrolytes. The substances that are commonly used as protective colloid include gelatin, albumin, agar, casein, gum arabic, glue, starch etc.

Sols of gold and other metals, dyes, ink etc. become very stable in presence of some stabilisers added in small amounts. Zsigmondy introduced the term "gold number" to measure the protective action of colloids.

The number of milligrams of the protective colloid that just prevents the change of colour when 1 cc of the standard salt solution is added to 10 cc of the standard gold sol is known as the gold number.

It should be noted from the above definition that the protective colloid having the least weight, that will prevent the change of colour of the gold sol, has the greatest protective value. It may be noted that gold number is not a very accurate constant for a colloid. The reciprocal of gold numbers are used to express the direct protective ratio. The values of gold numbers and reciprocal gold numbers for some substances are given in Table 19.4.

TABLE 19.4.

Gold numbers and reciprocal gold numbers of certain substances

Protective colloid	*Gold number*	*Reciprocal gold number*
Gelatin	0.005—0.01	200.0—100.0
Dextrin	6.0—20.0	0.17—0.05
Gum arabic	0.15—0.5	6.7—2.0
Albumin	0.1—0.2	10 - 5.0
Potato starch	25	0.04

Protective action is a very important phenomenon. It enables colloids to be kept for a long time when otherwise spontaneous change would take place. Carey Lea prepared silver sols by reducing silver nitrate with mixtures of ferrous sulphate and sodium citrate. It contains 99 per cent silver. Such sols are used in medicine for intravenous injection or as an ointment.

In the preparation of ice cream, little gelatin when added as a protective colloid gives the cream a smooth paste. Besides gold number, the iron number in which sols of Fe_2O_3 are used and the rubin number, which involves sols of congo red, have also been introduced to measure the protective characteristics of substances.

19.8. EMULSIONS

An emulsion is a liquid-liquid suspension, that is small drops of one liquid dispersed in another liquid. Emulsions are of very common occurrence in nature, the common examples are milk and mayonnaise. In most emulsions, one of the liquids is water and the other liquid is immiscible with water such as an oil or fat. When aniline is distilled in steam or an organic liquid, in alcohol or acetone be poured into excess of water, we get the emulsion "oil in water" type. In this case we have a few drops of oil dispersed in water. The term "oil" is used to represent the organic substance insoluble in water. If on the other hand, water is in the form of droplets dispersed in liquid fat, these emulsions are known as "water in oil" type. The type of emulsion that results on agitation of two liquids depends on the relative proportion of the two in the mixture. In order to stabilise an emulsion a third substance known as an emulsifying agent is added. A stable emulsion may be defined as a substance in which the globules retain their initial character and remain uniformly distributed throughout the continuous phase. The various deviations from this ideal behaviour are

() Breaking or cracking. This involves coalescence of the dispersed globules and produces eventual separation of the emulsion into two phases.

(*ii*) **Creaming**. This involves the concentration of the dispersed globules in either the upper or lower layers of the emulsion. It is caused by the influence of gravity on the globules since they usually have a different density from that of the continuous phase.

(*iii*) **Coagulation or flocculation**. This involves globules aggregating into loose masses within the emulsion. The globules do not coalesce and may be redispersed on shaking. Thus flocculation is less serious than breaking.

The properties of emulsions are influenced by the effectof impurities and added substances due to interfacial tension. The emulsifying agent reduces the interfacial tension. The most commonly used emulsifying agents are soap, long chain sulphonic acids and sulphates which are classified as detergents. The cleansing action of soap can be ascribed to the formation of an emulsion with oil, grease and water. Emulsions are usually opaque owing to the difference in refractive index between the two liquids and the droplets in emulsion are often negatively charged. Emulsions may be broken into two separate liquid layers by the process known as demulsification. The conversion of cream into butter by churning is an example of demulsification.

19.9. GELS

There are some sols that have a high concentration of dispersed solid and change spontaneously into a semi-solid form known as a gel. For example, gelatin dissolves in warm water forming a colloidal solution which when cooled sets to a jelly. Gels are formed by the interlocking of the dispersed particles in the form of a loose framework inside which liquid dispersion medium is contained. On the basis of their mechanical properties, gels can be classified into three types.

(*i*) **Elastic gels**. They possess the property of elasticity, *i.e.*, their shape is altered by applying a small force and is restored to the original shape when the force is removed. The examples of elastic gels are starch, gelatin, fruit jam and jellies. The molecules are held up by electrostatic forces between the ionised or polar groups.

(*ii*) **Rigid gels**. The best known example of this type is that of silicic acid, known as silica gel. A network of chemical bonds gives them a rigid structure.

(*iii*) **Thixotropic gels.** Such gels become semi-solid when at rest but become liquid when vigorously agitated. Kieselguhr and water form a thin paste when tilted slowly. The mixture does not flow but flows readily on shaking Solutions of some high polymers exhibit these properties. These are held up by weak attractive forces.

The term gel represents a physical state with properties intermediate between those of solids and liquids. The gels should satisfy the following criteria:

(*i*) They are coherent colloidal systems of at least two components (the gelling agent and a fluid component).

(*ii*) They exhibit mechanical properties characteristic of the solid state.

(*iii*) Each component is continuous throughout the system.

These criteria are fulfilled by gelatin, agar and bentonite gels in which the fluid component is aqueous, and by soft paraffin in which the fluid component is an organic liquid.

Many gels shrink if the fluid component is removed *e.g.*, by evaporation or freeze-drying. The remaining solid which will swell and reform the gel on contact with fresh fluid component is termed a Xerogel. Gelatin sheets, acacia tears, starch grain and leather are all xerogels.

The Structure of Gels

The rigidity of a gel arises from the presence of a network formed by the interlinking of particles of the gelling agent. The nature of the particles and the type of force that is responsible for the linkages determines the structure of the network and the properties of the gel.

The individual particles of a hydrophilic colloid may consist of either spherical or anisometric aggregates of small molecules or single macromolecules. The forces of attraction responsible for the linkages between gelling agent particles may range from strong primary valencies, as in silicic acid gels, to weaker hydrogen bonds and van der Waals forces. The weaker nature of these latter forces is indicated by the fact that a slight increase in temperature often causes liquefaction of a gel. Systems that exhibit this type transition such as agar and gelatin gels are termed as thermal gels. In addition the transition from gel state to a colloidal dispersion may in some cases be brought about by mechanical agitation. The systems exhibiting such type of transition are called thixotropic gels. The common examples are bentonite and aluminium hydroxide gels.

Properties of Gels

(*i*) **Swelling**. If a xerogel is placed in contact with a liquid that solvates it, then an appreciable amount of the liquid is often taken up and the volume of xerogel increases. This is called swelling. The degree of swelling depends on the number of linkages between individual molecules of gelling agent and on the strength of these linkages. For example in a protein xerogel, swelling is at a minimum at the iso-electric point of the protein because the intermolecular linkages are strongest at this point and, therefore offer more resistance to swelling. The presence of ions influence the degree of swelling.

(*ii*) **Syneresis**. Gel will often contract spontaneously and exude some of the fluid medium. This effect is known as syneresis and the degree to which it occurs usually decreases as the concentration of the gelling agent increases. Blood clot is a common example of a system that exhibits syneresis.

(*iii*) **Ageing**. Colloidal systems usually exhibit slow spontaneous aggregation. This is referred to as ageing. In gels, ageing results in the gradual formation of a denser network of gelling agent.

(*iv*) **Rheological properties**. Gels exhibit the mechanical properties of rigidity, tensile strength, and elasticity that are characteristic of solids. In thixotropic gels, these effects are only apparent below the yield value, above which the system exhibits the flow properties of suspensions.

Application of Gels

Gelatin gels are employed in the preparation of hard and soft capsules that may be used to mask the unpleasant tastes of solids and liquids. Agar and gelatin gels are used as solid media for the culture of micro-organisms. The diffusion of antibiotics, antiseptics, vitamins and enzymes through solid culture media is used in microbiological assay of these materials.

19.10. APPLICATIONS OF COLLOIDS

There are a number of important processes in which colloids play an important role.

(*a*) A very useful application is in Cottrell precipitation, as purification process for industrial smoke. The air near the factories and industrial plants is frequently contaminated with smoke and gases which result from the manufacturing processes. The smoke is laden with colloidal particles, such as cement dust, arsenic compounds and metallic powder, which are irritating and even poisonous. The Cottrell precipitator (Fig. 19.9) removes colloidal particles from the flue gases by means of electrical precipitation. In the Cottrell precipitator, flue gases are passed over wires maintained at high voltage where suspended particles acquire an electric charge. A collecting plate of opposite charge attracts the charged particles which loose their charge and fall to the bottom. The air pollution is thus reduced to a minimum.

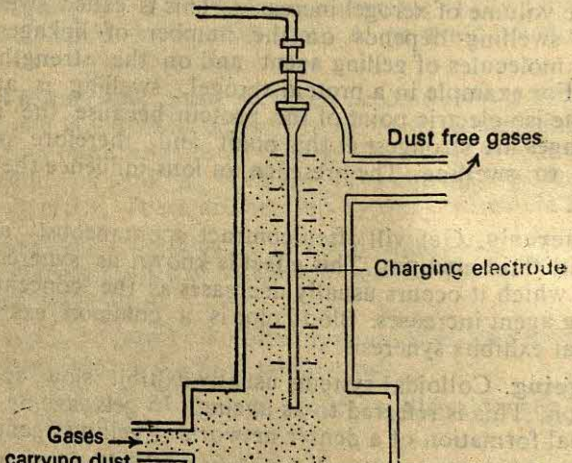


Fig. 19.9. Cottrell precipitator.

(*b*) Leather tannin is a process which utilises colloidal properties. Raw hides contain giant molecules arranged in long tangled fibres. Tanning materials which include tannin and compounds of chromium and aluminium are in colloidal state and the positively charged protein fibres adsorb negative charges from these metallic ingredients.

(*c*) In textile dyeing, colloidal substances called *mordants* are used to fasten dyes.

(*d*) In purification of water, aluminium sulphate and lime are added to form a flocculant precipitate of aluminium hydroxide. This precipitate will adsorb very fine particles of clay or other suspended matter and carry them to the settling tanks or basins. The reaction can be symbolised as

$$Al_2(SO_4)_3+3Ca(OH)_2=2Al(OH)_3\downarrow+3CaSO_4$$

(*e*) Formation of Deltas. Extensive deposits of silt or clay formed at the mouths of rivers by colloidal action are called *deltas.*

(*f*) The cleansing action of detergents is due to former's emulsifying properties. They form an emulsion with oil and dirt particles in water.

(*g*) Sewage usually contains considerable amounts of deflocculating substances such as soap, organic matter and the like which tend to keep it full of colloidally dispersed particles. The successful treatment of sewage, backwaters and trade effluents involves the separation from them these colloids by coagulation, adsorption, filtration or destruction (usually by bacteria in the septic tank).

(*h*) Smoke screens consist of titanium dioxide particles dispersed in air, and are used in warfare for the purpose of concealment.

(*i*) "Fire-foam" is a carbon dioxide froth made by mixing solution of sodium bicarbonate and alum. A protective colloid such as glue, dextrin or saponin is added to stabilise the foam and keep the bubbles in finely dispersed foam.

(*j*) Colloids are of great importance in living systems, for protoplasm itself is a gel. It contains considerable amount of protein, glycogen and phospholipid; all are lyophilic materials. Molecules of these substances exhibit imbibtion, that is they attract water strongly and so firmly that the water is said to be bound. This water cannot even freeze. When the particles in colloids rearrange and force some of the bound water out, syneresis is said to occur. In the digestive track, bile salts serve as agents to convert temporary aqueous oil emulsions to more permanent ones. It has been suggested that the efficiency of certain substances used in pharmaceutical preparations may be increased if colloidal forms are used, since these have large surface areas; for example the adsorption of toxins from the gastro intestinal tract by kaolin and the rate of neutralisation of excess acidity in stomach by aluminium hydroxide may be increased if these compounds are used in colloidal forms.

The use of colloidal iron and colloidal iodine is said to alter the effect of these compounds.

Blood plasma substitutes are colloidal dispersions in which the particle size is such that they are retained in the blood vessels for an adequate time. Colloidal gold, calcium and silver are used in medicines or as ointment.

19.11. ADSORPTION

When solids are allowed to remain in contact with a gas, a film of gas molecules accumlates on the surface. It was pointed out in the discussion of surface tension that the molecular forces at the surface of a liquid are unbalanced or unsaturated than in the bulk. Similarly, molecules or ions at the surface of a solid have unsaturated or residual forces. Solid and liquid surfaces, therefore, have a tendency to satisfy their residual forces by attracting onto and retaining on their surfaces, molecules of gases or other substances with which they come in contact. This results in higher concentration of molecules on the surface of a solid or liquid than in the bulk of the medium. This phenomenon is known as *adsorption*.

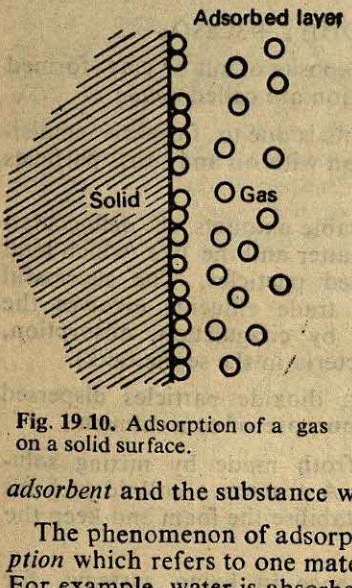


Fig. 19.10. Adsorption of a gas on a solid surface.

The substance on which the adsorption takes place is known as the *adsorbent* and the substance which is adsorbed is known as *adsorbate*.

The phenomenon of adsorption should not be confused with *absorption* which refers to one material passing into the bulk of another. For example, water is absorbed by a sponge and water vapors are adsorbed by anhydrous calcium chloride. On the other hand, water vapors are adsorbed by silica gel and acetic acid in solution is adsorbed by charcoal. When one is in a fix to decide whether a particular process is adsorption or absorption, the term *sorption* is used which includes both absorption and adsorption.

Figure 19.10 shows the adsorption of a gas on a solid surface.

19.12. ADSORPTION OF GASES BY SOLIDS

All solids adsorb gases to some measurable extent. The magnitude of adsorption of gases by solids depends on the nature of the solid and the gas being adsorbed, the state of subdivision (area) of the solid the temperature and the pressure of the gas.

It has been observed that those solids which have the largest possible surface areas are very good adsorbing agents. In fact, larger is the surface area, greater will be the amount of gas adsorbed. The best adsorbents used in practice are various kinds of specially prepared carbon (wood, bone and blood charcoals etc.) They have large surface areas due to their exceptionally high porosity. In addition to various kinds of carbon, other good adsorbing substances are silica gel, alumina, kaolin and certain aluminosilicates. The adsorption power of these substances can further be enhanced by a process called activation. During activation, the adsorbent is heated in steam or air atmosphere to about 1500°C. Heating drives out all impurities gasified at that temperature from the pores and leads to larger free surface for adsorption. Thus, activated charcoal at 24°C adsorbs 1.48 gram of carbon tetrachloride per gram of charcoal whereas before activation it, could adsorb only 0.011 gram per gram of charcoal.

Gases which condense more easily are much more strongly adsorbed. Since it is difficult to determine the surface area of adsorbing agents directly, the mass of adsorbent is generally taken as a measure of the surface available for adsorption. Hence adsorption is generally expressed as the amount of substance adsorbed per unit mass of adsorbing agents.

The amount of adsorbed gas, as a rule. decreases with increase of temperature at a constant pressure and increases with a fall in temperature. Hence, according to Le-Chatelier Braun principle, adsorption of a gas by a solid is accompanied by evolution of heat which is known as the *heat of adsorption.* This has been confirmed by direct experimental evidence. For every gas and solid, there is some definite heat of adsorption.

The extent of adsorption increases with increase of pressure.

19.13. TYPES OF ADSORPTION

The type of force that holds the adsorbed molecules on the surface has a considerable effect on certain characteristics, in particular how tightly the molecules are held and whether the solid will adsorb certain substances more strongly than others. There are two types of adsorption:

(*a*) Physical or van der Waals adsorption.

(*b*) Chemisorption or activated adsorption.

Physical adsorption. It is characterised by low heats of adsorption of the order of 5 to 10 kcal per mol of the gas. The process of adsorption is similar to the condensation of gas on liquid. This suggests that the forces by which the adsorbed gas molecules are held to the surface of the solid, are similar to the forces of cohersion of molecules in the liquid state. A rise in temperature will increase the kinetic energies of molecules and the molecules will leave the surface thus lowering the extent of adsorption. Another characteristic of physical adsorption is that the adsorption equilibrium is reversible and is established rapidly. Physical adsorption is generally observed in the adsorption of various gases on charcoal and is independent of the chemical nature of the substance being adsorbed.

Chemisorption. In chemisorption, adsorption occurs by chemical force and a chemical bond is formed between the adsorbed molecule and the surface. Chemisorption is thus highly selective since only certain types of molecules will be adsorbed by a particular solid. This depends on the chemical properties of gas and the adsorbent. Chemisorption is accompanied by much higher heat changes from 10 kcals to 100 kcals per mole. These heat changes are of the same order as those involved in chemical reactions. Unlike physical adsorption, chemical adsorption is not reversible. Hydrogen is strongly adsorbed by the metals—nickel, iron and platinum.

In many cases, it has been observed that adsorption is neither physical nor chemical but a combination of the two. Some systems show physical adsorption at low temperatures but as the temperature is raised, physical adsorption changes into chemical adsorption.

19.14. ADSORPTION ISOTHERMS

A plot obtained between the amount of substance adsorbed per unit mass of the adsorbent and the equilibrium pressure (in case of a gas) or concentration (in case of solution) at constant temperature is known as the adsorption isotherm. Five different types of adsorption isotherms have been observed in the adsorption of gases on solids. These are shown in Fig. 19.11 on next page.

p^0=pressure required to condense the gas to liquid.

Type I. Adsorption of Nitrogen on charcoal at —183°C.

Type II. Adsorption of nitrogen on Iron or silica gel at —195°C.

Type III. Adsorption of Bromine or Iodine on silica gel at 83°C.

Type IV. Adsorption of Benzene vapors on ferric oxide gel at 50°C.

Type V. Adsorption of water vapors on charcoal at 100°C.

In case of chemisorption, only Type I curves are obtained while in case of physical adsorption, all the five isotherms are observed.

19.15. EXPLANATION OF TYPE I ISOTHERM

The Freundlich adsorption Isotherm. To show the variation of the amount of gas adsorbed per unit mass of the adsorbent with pressure at constant temperature, Freundlich suggested an empirical equation which is known as Freundlich's adsorption isotherm. The equation is

$$\frac{x}{m}=kp^{1/n} \qquad \ldots (19.1$$

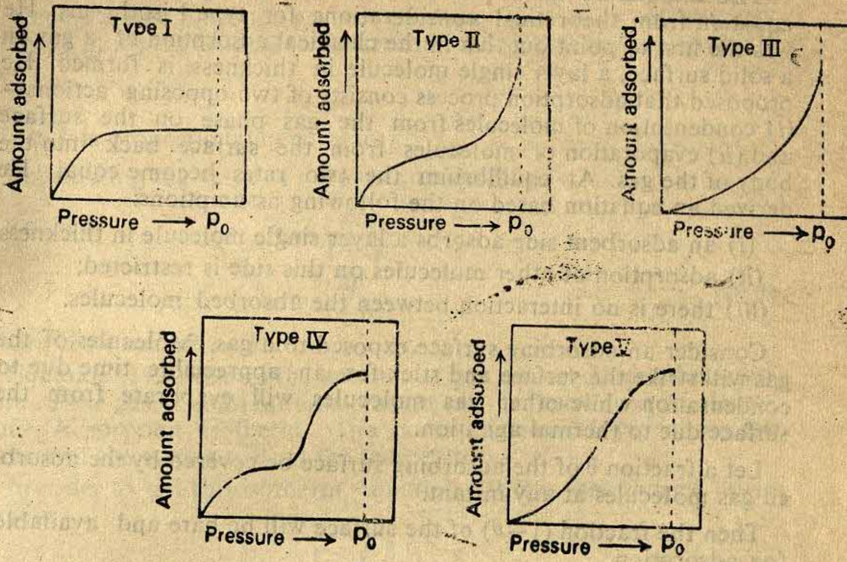


Fig. 19.11. Five types of adsorption isotherms.

where x is the mass of gas adsorbed, m the mass of the adsorbent, p is the equilibrium pressure and k and n are constants which depend on the nature of the absorbate and adsorbent and on the temperature. This equation is applicable only at low pressures. In order to test equation (19.1), take the logarithms of both sides, when it will take the form

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p \qquad \ldots (19.2)$$

According to equation (19.2), a plot of log $\frac{x}{m}$ against log p should be a straight line with slope equal to $\frac{1}{n}$ and intercept log k as shown in Fig. 19.12.

It was found that the actual plots were straight lines only at low pressures and showed a slight curvature at higher pressure, especially at low temperatures. This indicates that equation (19.1) is approximate and cannot be regarded an equation of general applicability to explain adsorption of gases by solids.

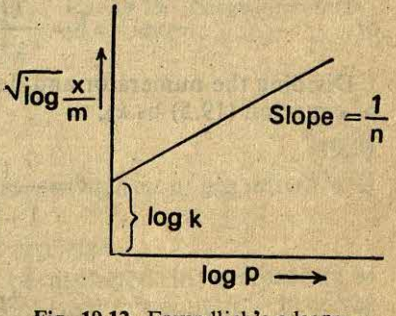


Fig. 19.12. Freundlich's adscrption isotherm.

The Langmuir adsorption isotherm. Langmuir derived an equation from theoretical considerations for type I isotherms. He was the first to point out that in the chemical adsorption of a gas on a solid surface, a layer single molecule in thickness is formed. He proposed that adsorption process consists of two opposing actions—(*i*) condensation of molecules from the gas phase on the surface and (*ii*) evaporation of molecules from the surface back into the body of the gas. At equilibrium the two rates become equal. He derived an equation based on the following assumptions:

(*i*) an adsorbent side adsorbs a layer single molecule in thickness;
(*ii*) adsorption of other molecules on this side is restricted;
(*iii*) there is no interaction between the absorbed molecules.

Consider an adsorbing surface exposed to a gas. Molecules of the gas will strike the surface and stick for an appreciable time due to condensation while other gas molecules will evaporate from the surface due to thermal agitation.

Let a fraction θ of the adsorbing surface be covered by the adsorbed gas molecules at any instant.

Then the fraction $(1-\theta)$ of the surface will be bare and available for adsorption.

If p is the pressure of the gas, then from kinetic theory of gases, rate of adsorption of gas molecules

$$=k_1p(1-\theta) \qquad \ldots (19.3)$$

where k_1 is proportionality constant.

The rate at which gas molecules evaporate from the surface will depend on the fraction of the surface covered by the gas molecules.

Therefore, rate of evaporation of gas molecules

$$=k_2\theta \qquad \ldots (19.4)$$

where k_2 is another proportionality constant.

At equilibrium, the two rates must be equal so that

$$k_1p(1-\theta)=k_2\theta$$

or

$$\theta=\frac{k_1p}{k_2+k_1p} \qquad \ldots (19.5)$$

Dividing the numerator and denominator of the right hand side of equation (19.5) bs k_2,

$$\theta=\frac{(k_1/k_2)p}{1+\left(\frac{k_1}{k_2}\right)p}$$

or

$$\theta=\frac{bp}{1+bp} \qquad \ldots (19.6)$$

where b is another constant and is equal to k_1/k_2.

Since the amount of the gas adsorbed per unit mass of the adsorbent, y, is proportional to the fraction θ of the surface covered, *i.e.*,

$$y=k\theta$$

where k is proportionality constant.

Substituting the value of θ from equation (19.6)

$$y=\frac{kbp}{1+bp}$$

$$=\frac{ap}{1+bp} \qquad \ldots (19.7)$$

where the constant $a=kb$.

Equation (19.7) relates the amount of gas adsorbed to the pressure of the gas at constant temperature and is known as the Langmuir Adsorption Isotherm. The constants a and b depend on the nature of the system and on the temperature.

In order to test this isotherm, equation (19.7) is rearranged so as to give

$$\frac{p}{y}=\frac{1}{a}+\left(\frac{b}{a}\right)p \qquad \ldots (19.8)$$

This equation is similar to an equation for a straight line. Hence if p/y is plotted against p, a straight line should be obtained with a slope equal to b/a and intercept equal to $1/a$ as shown in Fig. 19.13.

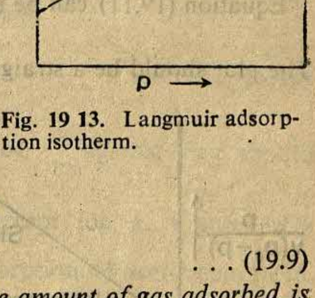


Fig. 19 13. Langmuir adsorption isotherm.

It was observed in numerous cases that actual curves were straight lines thus verifying Langmuir adsorption equation.

Consider two extreme cases of Langmuir Isotherm:

Case I. *When the gas pressure p is very small.*

Under these conditions, the factor bp is negligibly small as compared to unity in the denominator of equation (19.7). This equation, therefore, becomes

$$y=ap$$

or

$$y \propto p \qquad \ldots (19.9)$$

which means that at *very low pressures, the amount of gas adsorbed is directly proportional to the pressure.*

Case I. *When the gas pressure p is very high.*

Under these conditions, unity can be neglected in comparison to bp in the denominator of equation (19.7) and this equation becomes

$$y=\frac{a}{b} \qquad \ldots (19.10)$$

which means that *at very high pressure, the amount of gas adsorbed reaches a constant limiting value.*

This situation arises when the surface is nearly completely covered with a monomolecular layer at high pressures so that change in pressure has a little effect on the amount of gas adsorbed.

Restriction. Langmuir equation is applicable for smooth, non-porous surfaces, which are not very good adsorbents, and for low values of pressure. If the surface is a very good adsorbent and pressure is very high, there are chances of multilayer formation.

19.16. TYPE II-V ISOTHERMS

It was pinted out earlier that in physical adsorption, all the five types of adsorpsion isotherms are observed. Although Langmuir isotherm can satisfactorily explain type I isotherm, it altogether fails to explain all the five types of curves. It was proposed that in types II, and III, multilayer formation takes place especially as the gas pressure is increased. On this assumption, Brunauer, Emmett and Teller derived the B.E.T. equation for types II and III isotherms. The equation is

$$\frac{p}{v(p_0-p)}=\frac{1}{v_m c}+\frac{(c-1)}{(v_m c)}\cdot\frac{p}{p_0} \qquad \ldots (19.11)$$

where v and v_m are the volumes, reduced to standard conditions, of the gas adsorbed at pressure p and when the surface is covered with a monomolecular layer respectively at temperature T, p_0 the saturated vapor pressure of the gas at temperature T and c is a constant approximately equal to $e(E_1-E_L)/RT$ where E_1 is the heat of adsorption of the first layer and E_L is the heat of condensation of the gas to liquid. If $E_1>E_L$, isotherms of type II are observed and if $E_1<E_L$ isotherms of type III are observed.

Equation (19.11) can be tested by plotting $\frac{p}{v(p_0-p)}$ versus $\frac{p}{p_0}$. The plot should be a straight line with slope $\frac{c-1}{v_m c}$ and intercept $\frac{1}{v_m c}$ as shown in Fig. 19.14.

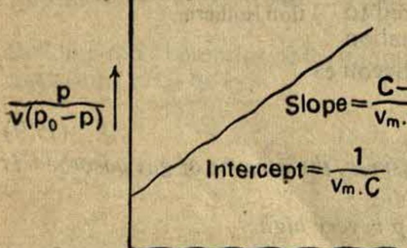


Fig. 19.14. Isotherm plot according to B.E.T. equation.

To explain type IV and V isotherms, it was suggested that in addition to the multilayer adsorption, condensation of the gas molecules also takes place in the small pores and capillaries of the adsorbent even at pressures below p_0. The distinction between these two types is again based on the relative magnitudes of E_1 and E_L. If $E_1>E_L$, type IV isotherms are observed and if $E_1 < E_L$, type V isotherms are observed.

19.17. ADSORPTION FROM SOLUTION

Solid surfaces can also adsorb solutes from the solution. An application of adsorption from solution is the use of activated charcoal for decolorising sugar solutions. Activated charcoal can adsorb colouring impurities on its surface. Other examples of this type of adsorption are the adsorption of ammonia from ammonium hydroxide, phenolphthalein from solutions of acids or bases and acetic acid from its solution in water, etc. by activated charcoal.

It has been observed that carbon adsorbs non-electrolytes more readily from a solution than electrolytes and inorganic solids adsorb electrolytes in preference to non-electrolytes. This behaviour of adsorbents to attract certain substances in preference to other substances leads to a phenomenon of *negative adsorption i.e.*, concentration of the solute becomes more after treatment with the adsorbent.

Adsorption from solution in most of the cases leads to the formation of layer single molecule in thickness on the surface of the solid as was observed in the chemisorption of gas on a solid.

This type of adsorption is also affected by temperature and concentration. The extent of adsorption decreases with increase of temperature and increases with increase of concentration. In order to represent the variation of extent of adsorption with concentration, Freundlich suggested an empirical isotherm similar to equation (19.1). This equation is,

$$\frac{x}{m} = kc^{1/n} \qquad \ldots (19.12)$$

where x and m are the masses of the substance adsorbed and of adsorbent respectively, c is the equilibrium concentration of the adsorbed substance in the solution, k and n are empirical constants. Taking logarithms of equation (19.12) we get,

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log c \qquad \ldots (19.13)$$

Equation (19.13) implies that a plot of log $\frac{x}{m}$ against log c should be a straight line with slope $\frac{1}{n}$ and intercept log k. Figure 19.5 shows such a plot of a data for the adsorption of acetic acid from aqueous solution at 25°C.

19.18. APPLICATIONS OF ADSORPTION

Adsorption finds extensive application both in the laboratory and in the industry. Some of the important applications are:

(*i*) Adsorption of gases on solids is employed for creating a high vacuum between the walls of Dewar containers designed for storing liquid air or liquid hydrogen. This is achieved by placing activated charcoal between the walls which has already been exhausted to the maximum extent using a vacuum pump. The activated charcoal will adsorb any gas which may appear due to glass imperfection or diffusion through the glass.

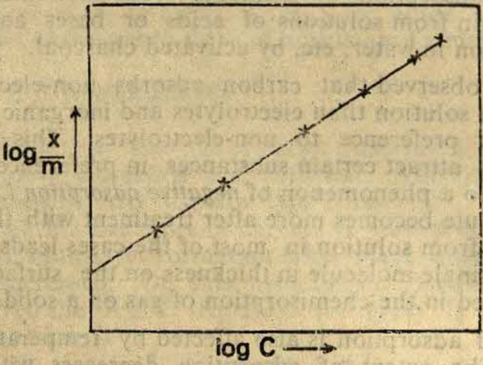


Fig. 19.15. Adsorption of acetic acid by charcoal.

(*ii*) Adsorption of gases on solids is also utilised in gas masks which contain an adsorbent or a series of adsorbents. These adsorbents purify the air for breathing by adsorbing all the poisonous gases from the atmosphere. In the same manner, suitable absorbents can also be employed in the industry for recovering the solvent vapors from air or particular solvents from the mixture of other gases.

(*ii*) Charcoal finds an extensive application in the sugar industry. It is used as a decoloriser for the purification of sugar liquors. It can also be used for removing coloring matter from various other types of solutions.

(*iv*) Adsorption is employed for the recovery and concentration of vitamins and other biological substances.

(*v*) Adsorption finds extensive application in chromatography which is based on selective adsorption of a number of constituents present together in a solution or gas.

(*vi*) Adsorption also plays an important role in catalysis (see the chapter on Catalysis.)

PROBLEMS

1. Select the examples most likely to correspond to each type of colloid listed.

(A) ammonium chloride in the laboratory atmosphere, (B) gelatin, (C) homogenized salad dressing, (D) household deodorising spray, (E) Jello in hot water, (F) Pumice, (G) shaving leather

(*a*) aerosol fog
(*b*) aerosol smoke
(*c*) liquid foam
(*d*) solid foam
(*e*) emulsion
(*f*) gel
(*g*) sol

Ans. (*a*) (D); (*b*) (A); (*c*) (G); (*d*) (F); (*e*) (C); (*f*) B; (*g*) (E).

2. Classify the following colloidal systems.

(*a*) Ivory soap.
(*b*) microscopic pollen grains in air.
(*c*) homogenised oil and vinegar salad dressings.
(*d*) an aqueous dispersion of a solid detergent.
(*e*) whipped cream.

Ans. (*a*) (solid) foam, (*b*) aerosol (*c*) emulsion, (*d*) sol (liquid) foam.

3. Indicate the main factor (surface charge, rigidity or other factors) that probably contribute to the stability of each of the following systems. "Other factors" includes, Brownian motion, slow sedimentation rates and thermal convection currents.

(*a*) an emulsion of oil in soapy waters.
(*b*) a black diamond.
(*c*) homogenised milk.
(*d*) an antimony sulphide sol prepared by precipitation in alkaline solution.
(*e*) a marshmallow.

Ans. (*a*) surface charge (*b*) rigidity (*c*) other factors (*d*) surface charge (*e*) rigidity.

4. What do you understand by the colloidal state of matter? Bring out the difference between a colloidal solution and a true solution.

5. What are different types of methods for the preparation of colloids? How would you prepare a colloidal solution of (*a*) Gold (*b*) Arsenious sulphide (*c*) Sulphur.

6. Explain the use of (*a*) dialysis (*b*) electro-dialysis (*c*) ultrafiltration in the purification of colloidal solutions.

7. Distinguish between lyophobic and lyophillic colloids. Describe Bredig's arc method for the preparation of lyophobic colloids.

8. Explain why:

(*a*) A colloidal solution is not precipitated on the addition of an electrolyte in presence of gelatin.

(*b*) Alum is used in town water supply.
(*c*) The sky looks blue.
(*d*) A colloidal solution contains electrically charged particles.

9. Write short notes on the following:

(*a*) Brownian movement
(*b*) Cataphoresis
(*c*) Gold number
(*a*) Coagulation by electrolytes.

10. Write notes on the following:

(*a*) Artificial rain

(*b*) Cottrell smoke precipitator

(*c*) Tyndall effect.

11. What are emulsions? How are they classified? Give one method for their preparation.

12. Explain the difference between absorption and adsorption. Discuss the types of adsorption isotherms.

13. Write notes on the following:

(*a*) Freundlich adsorption isotherms.

(*b*) Langmuir adsorption isotherms.

14. Explain the qualitative features of B.E.T. equation. What is meant by chemisorption?

15. Write notes on:

(*a*) Gels

(*b*) Adsorption from solution

(*c*) Chromatography

(*d*) Uses of colloids

(*e*) Schulze-Hardy Law.

Chapter 20

ATOMIC STRUCTURE

20.1. INTRODUCTION

Speculations concerning the possible atomic nature of matter are found in the writings of Hindu and Egyption philosophers living many centuries before the birth of Christ. In the fifth century Democritus strongly advocated the concept that matter was ultimately composed of tiny individual particles and coined the word 'atoms' for them. They believed that the material of a growing plant is composed of water and stone atoms provided by the soil, atoms of fire supplied the rays of the sun. In the modern terminology the Greek formula for wood would be *SWF*. The drying of wood was considered to be escape from wood of water atoms *i e*. $SWF \rightarrow SF + W$, the burning of wood, the decomposition of dry wood into fire atoms and stone atoms $SF \rightarrow S + F$. We now know that these views were quite wrong.

The first statement of an atomic theory based on the experimental evidence was that of John Dalton, published in 1807. The experimental observations that led Dalton to his statement, were the Laws of Chemical Combination, which summarised the then known facts about the proportions by mass in which the elements combine to form compounds. Dalton's atomic theory can be stated in modern terms as follows:

(*i*) Atoms are the ultimate, discrete particles of matter which are not subdivided during the course of chemical changes. They can not be created or destroyed.

(*ii*) All atoms of any element are identical in all respects, including mass, and different from the atoms of other elements.

(*iii*) Compounds are formed by the combination of atoms of different elements in simple, integral numerical proportions forming the compound atoms (or molecules) of such compounds.

20.2. THE ELECTRICAL NATURE OF THE ATOM

In 1791, the Italian physician, Luigi Galvani made the accidental discovery that a freshly dissected frog's leg gave a sharp convulsion when brought into contact with a discharging static electricity machine. The effect was more pronounced when two different metals were used to complete the circuit. Because of his biological inclinations, Galvani thought the phenomenon to be characteristic only of living materials and named it 'animal electricity'. The development of the modern theory of atomic structure began with the concept of electronic charge first introduced by Faraday from his Laws of Electrolysis. A brief mention of these laws will be given in this section. For a detailed study of these laws refer to Section 14.3. The mass of a substance deposited or collected on the electrodes is directly proportional to the quantity of electricity passed through the electrolytic solution. This law which is known as Faraday's first law suggests that each ion of a given chemical substance carries a well defined electric charge.

Later on Faraday investigated the relative amounts of electric charge carried by ions of different chemical substances. He passed an electric current through the solutions of several different substances *e.g.*, nitric acid, silver nitrate and copper sulphate as shown in Fig. 20.1.

As a result of electrolysis in the case of nitric acid, hydrogen gas is evolved on the cathode, while certain amounts of silver and copper are deposited in the case of silver nitrate and copper sulphate solutions respectively. On comparing the amounts of silver liberated by the same electric current flowing for the same length of time with that of copper liberated by the same electric current for the same duration, it is found that the weight ratio of silver to copper is 3 : 40 instead of 1 : 70. From this ratio, it can be concluded that one ion of copper carries twice as much electricity of one ion of silver or, in other words, silver has lost one electron, while the copper has lost two electrons. The quantity of electricity required to evolve one equivalent of any substance is 96,500 coulombs, also known as one Faraday.

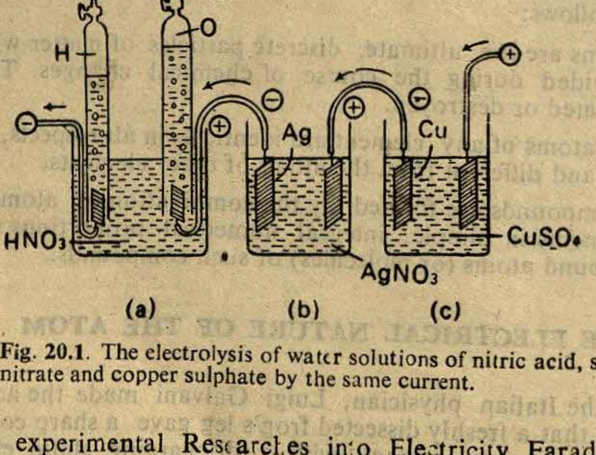


Fig. 20.1. The electrolysis of water solutions of nitric acid, silver nitrate and copper sulphate by the same current.

In his experimental Researches into Electricity Faraday wrote, "although we know nothing of what an atom is, yet we can not resist forming some idea of a small particle, which represents it to the mind; and although we are in equal, if not greater ignorance of electricity, so as to be unable to say whether it is a particular matter or matters or mere motions of ordinary matter, or some kind of third power or agent, yet there is immensity of facts which justifies us in believing that the atoms of matter are in some way endowed or associated with electrical powers, to which they owe their most striking qualities and among them their mutual chemical affinity."

A 60 cm long pyrex tube fitted with aluminium electrodes is used for the purpose. It is provided with a side tube T to communicate with a vacuum pump, No discharge occurs when a potential as high as 10,000 volts is applied at atmospheric pressure. Now if the pressure inside the tube is gradually decreased with the help of a vacuum pump, the discharge starts due to the ions produced by the electric field. As the pressure inside the discharge tube is about 1 mm of mercury a dark space is created near the cathode. This is known as Faraday's dark space. When the pressure inside the tube is lower than 0.01 mm a stream of rays is emitted from the cathode and are known as cathode rays.

Properties of Cathode Rays

Some of the important properties of cathode rays are as under:

(*i*) Cathode rays travel in straight lines and cast shadows of the objects placed in their path.

(*ii*) Cathode rays can produce mechanical effect. This is shown by the fact that a light paddle wheel placed in the path of the cathode rays is set in motion. This shows that cathode rays consist of material particles.

(*ii*) They are deflected by electric and magnetic fields from their straight path and carry a negative charge.

From the study of various properties of the cathode rays it appears probable that they consist of a stream of negatively charged particles emanating from the cathode with high speed. These particles are called *electrons* and the magnitude of the charge they carry is equal to the unit charge of electricity.

20.3. THE CHARGE-TO-MASS RATIO OF AN ELECTRON

Sir J.J. Thomson devised a method for determining the ratio of the charge to mass of an electron. This method is based on the principle that a moving electron has the characteristics of current and follows all the laws obeyed by a conductor carrying current when placed in a magnetic or electric field. The apparatus used by Thomson is shown in Fig. 20.2.

Consider a beam of electrons each of mass m and charge e moving with a velocity v in a straight line. The electric and magnetic fields were applied over the same span of path but at right angles to each other. In this arrangement, a beam of electrons from the

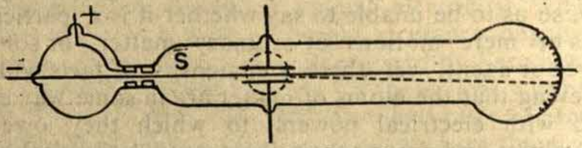


Fig. 20.2. J.J. Thomson's apparatus for the determination of $\frac{e}{m}$ of an electron.

cathode, after passing through the slit S, enters the magnetic and electric fields, and suffers deflection. The fields are adjusted to obtain the null point *i.e.* when the fields counter-balance each other, the beam goes undeflected and causes a fluorescent spot. From the relationships of the forces involved, the ratio of the electron charge e to its mass m may then be evaluated. Thomson's experiments gave approximate value of $\frac{e}{m}$. Modern measurements using more accurate techniques gave $\frac{e}{m} = 1.7588 \times 10^{11}$ C/kg.

20.4. THE CHARGE ON THE ELECTRON

R.A. Millikan in 1909 used fine oil drops in the cloud chamber to

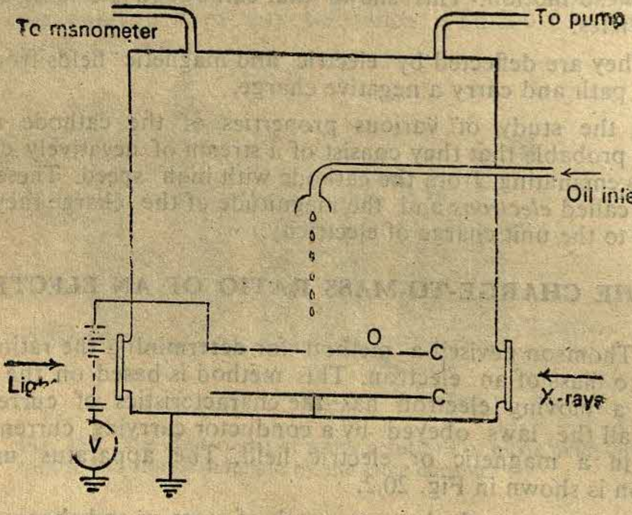


Fig. 20.3. Millikan's oil-drop method.

obtain the accurate value of charge *e*. The essential parts of the Millikan's oil-drop apparatus are shown in Fig. 20.3.

A fine spray of low pressure oil drops are produced by an atomiser. Some drops pass into the upper part of the chamber. Since the drops are extremely small they are illuminated by an arc lamp having the heat rays absorbing arrangement. The drops appear as bright spots when observed with the help of a telescope.

Either of the plate C and C_1 can be made positive with respect to one another and the movement of a particular drop is studied in this field with the help of telescope. When a drop of oil passes the hole O and enters the space between the plates the hole is closed and the drop acquires a charge due to the gaseous ions present inside the chamber. The electric field between the plates is adjusted in magnitude and sign so that the drop rises upwards. When the drop touches a fixed mark the field is then switched off and the drop starts falling down due to the force of gravity. This is allowed till the second fixed point. Thus the time for each drop is noted and the calculations are done on the following pattern.

When a drop of radius a falls under the action of gravity alone its weight is $\frac{4}{3}\pi a^3 \rho g$ where ρ is the density of the oil and g is the acceleration due to gravity. The upthrust due to the displaced air is given by $\frac{4}{3}\pi a^3 \rho_0 g$, ρ_0 is the density of the air. The viscous force acts as the retarding force on the drop as it moves through the air. This retarding force is given by Stokes as $6\pi \eta a v_0$ where η is the viscosity of air and v_0 the velocity of the drop. The two forces become equal when the velocity becomes uniform, *i.e.*,

$$\frac{4}{3}\pi a^3 (\rho-\rho_0)g = 6\pi \eta a v_0 \qquad \ldots (20.1)$$

When the electric field X is applied, the drop moves upward with a constant velocity v_X. The resultant force is zero as the velocity is uniform, *i.e.*,

$$\frac{4}{3}\pi a^3(\rho-\rho_0)g + 6\pi \eta a v_X = Xq$$

$$\therefore \qquad q = \frac{6\pi \eta a}{X}(v_0 + v_X) \qquad \ldots (20.2)$$

Millikan found that the values of q for different drops were always multiples of a common value e *i.e.*, $q = ne$ where n is an integer. The highest common factor from a large number of observations was taken to be the electronic charge e. This experiment illustrates the atomicity of electricity and the numerical value of the unit of electricity, e was found to be 1.602×10^{-19} columb. In the previous section $\frac{e}{m}$ was found to be 1.7588×10^{11} columb/kg, the mass m of the electron is given by 9.109534×10^{-31} kg. This is the rest mass of the electron.

20.5. MODELS OF ATOMIC STRUCTURE

In many cases we can explain a phenomenon or an object with the help of models. A model can become more and more sophisticated but it can never be the real thing. Take as an example the model of a boat. A child playing in a stream is satisfied with a stick of wood as a model boat. Later a boy sails a boat with a real sail, keel and rudder over a pond, The model may be constructed exactly to the scale, but it would still by its very nature be a model and not the real thing. The case of scientific models is very much the same, with the important distinction that the subject of the model is unseen and in one sense unknown. A model is used in this case to account for observations. For instance Dalton explained the constant composition of compounds by suggesting that matter was composed of atoms and that compounds consisted of combinations of atoms of elements in certain fixed ratios. He was proposing the atom as a model and his model of the atom was extremely simple Just how does one establish that one model is right and another wrong? Each model can be used to predict the results of various experiments. The one which predicts contrary to the experiment is thus rejected.

Thomson's Atomic Model

According to this model atoms consisted of a positively charged substance distributed uniformly over the entire body of the atom, with negative electrons imbedded in this continuous positive charge like seeds in a water melon (Fig. 20.4). Since electrons repel each other but are on the other hand attracted to the centre of the positive charge, they were supposed to assume certain stable positions inside the body of the atom. If this distribution were disturbed by some external force, such as, for example a violent collsion between two atoms in a hot gas the electrons were supposed to start vibrating around their equilibrium position, emitting light waves of corresponding frequencies. Attempts to correlate the emission frequencies, of electrons in Thomson's atom with actually observed frequencies of light emitted, did not prove to be successful. After a number of futile efforts it became rather clear that although Thomson's model considered an atom to be a complex system formed by positive and negative electric charges rather than an elementary indivisible body.

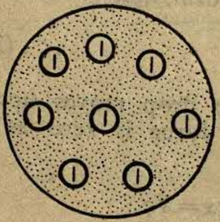


Fig. 20.4. J.J. Thomson Water-Melon model of the atom.

20.6. RUTHERFORD'S NUCLEAR MODEL OF THE ATOM

J.J. Thomson's static "water-melon mode" of the atom was transformed into a "dynamic planetary model" by his student Ernest Rutherford (1871-1937) from his well known scattering experiments. The experimental arrangement is shown in Fig. 20.5.

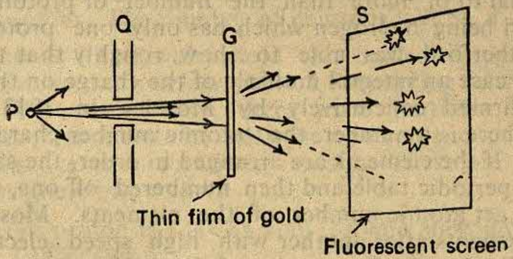


Fig. 20.5. Rutherford's scattering experiment.

The α-particles from a radioactive substance are narrowed down into a thin beam with a diaphragm *Q* and are allowed to fall on a thin foil of gold *G* of thickness 0.01 mm. The α-particles cause scintillations on the screen. In his experiment Rutherford observed that most of the α-particles passed through undeflected and only a few of them (one in 10,000) scattered through large angles.

From these observations he concluded that this was possible only if α-particles could collide with an extremely dense assembly of positive charge. He further developed the idea and said that whole of the positive charge of atom is concentrated in a very small sphere of diameter of the order of 10^{-12} cm. This volume in an atom where whole of the positive charge is concentrated was named nucleus. As the atom is neutral in itself, an equal number of electrons were assumed to be distributed around the nucleus in the empty space.

The above model of the atom was more satisfactory than the Thomson's model; but it suffered from a serious drawback. Since an electron rotating around the nucleus is attracted towards it, it must emit electromagnetic radiations. Hence, the electron will spiral down into the nucleus as shown in Fig. 20.6. Contrary to this we see experimentally that atoms, like hydrogen emit line spectra of a fixed wave length.

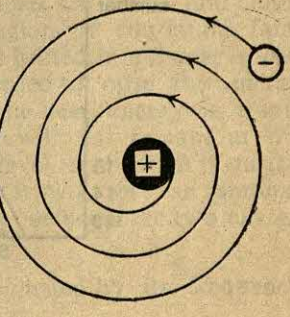


Fig. 20.6. Spiral path of the electron.

20.7. ATOMIC NUMBER

The objection as to how could close

packed stacking of protons could give a stable nucleus, found answer in the discovery of neutron by Chadwick in 1932. This had a mass=1 amu and charge=0. The mass of the nucleus will be the sum of the mass of protons and neutrons. The nuclear charge will be equal to the number of protons. The particles in the nucleus *i.e.*, neutrons and protons were collectively called nucleons. A study of various atomic nuclei shows that the number of neutrons in a nucleus is equal to or more than the number of protons in it, the only exception being hydrogen which has only one proton and no neutron. Rutherford was able to show, roughly that the positive charge was in case an integral multiple of the charge on the proton. This was confirmed conclusively by Moseley in 1913. Moseley showed that there is a number, the "atomic number characteristic of each element. If the elements are arranged in order, the same order as that of the periodic table and then numbered off-one, two, three, four, etc., we get atomic number of the elements. Moseley bombarded one elements after another with high speed electrons when they emitted X-rays, the frequencies of these X-rays proved in each case to be characteristic of the element bombarded. He observed frequency of the hardest X-rays emitted in each case *i.e.*, rays of greatest frequency. A graph was then plotted between the square roots of these greatest frequencies against the atomic numbers of the elements. The graph obtained was a straight line as shown in Fig. 20.7. The frequencies were thus related to the atomic numbers. Moseley thus showed that atomic number is a fundamental constant characteristic of the atom. The atomic number is equal to the number of positive charge on the nucleus.

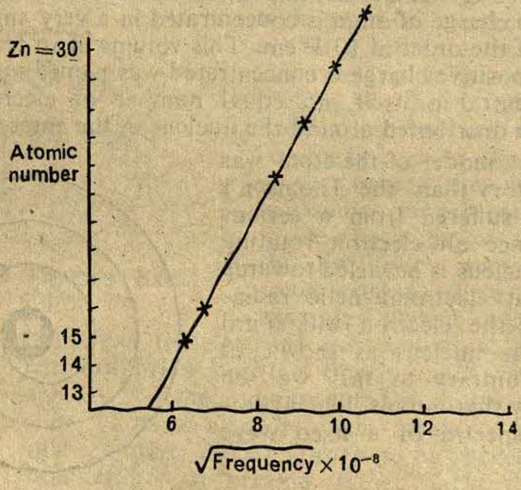


Fig. 20.7. The relation between X-ray frequencies and atomic numbers.

20.8. THE NUCLEAR CHARGE

The particles in the nucleus are collectively called *nucleons* and it consists of neutrons and protons. The shape of the nucleus is similar to a drop of liquid and has a radius of 2×10^{-13} cm. A. van den Brock (1913) suggested that the number of charges on the nucleus of an atom is equal to its atomic number. If an element has an atomic weight A and has an atomic number Z, its nucleus will consist of Z protons. The number of neutrons will be $A-Z$.

The nature of forces which hold the nucleons together is one of the main problems of nuclear physics. According to the theory suggested by Yukawa in 1935, there exist particles called *mesons* having mass intermediate between the electron and proton. Mesons were first discovered in cosmic ray studies. These are of two types and are designated as π and μ.

The mass of proton is 1.00758 amu (atomic mass unit) and that of neutron is 1.00899 amu.

20.9. ATOMIC SPECTRA

When an element is heated in a flame or a discharge of electricity is passed through a gas, colours of light characteristic of the element is seen. For example, discharge tubes containing neon gas at low pressure glow red, sodium light emits yellow light and mercury provides a greenish glow. This light when passed through a spectroscope produces a spectrum called *emission spectrum.* The emission spectrum thus obtained consists of a series of lines, called *line spectrum.* The line spectrum is also known as atomic spectrum since it originates in the atom of the element. Each element gives a unique pattern of spectral lines, and each line has a distinct wavelength.

The simplest spectrum is that of hydrogen, the simplest element. The part of the spectrum of hydrogen in the visible region consists of lines and the wavelengths of successive lines are closer and closer until they finally become a continuum, a region of continuous faint light. For example, when a sodium atom is heated in a flame, it can only absorb energy in the exact amount needed to raise the energy of an electron to some higher level. Thus the heat energy is transformed into electronic energy. The electron will not remain at the high level and it will fall back to the same level from which it started or to some intermediate level. In doing so, it will lose an amount of energy exactly equal to the difference between the two energy levels.

A spectral line of hydrogen might be designated by its frequency (ν) as well as its wavelength (λ) *i.e.*

$$\nu = \frac{c}{\lambda}\ \text{sec}^{-1}$$

where c is the velocity of light. The wave number $\bar{\nu}$ is defined as

$$\bar{\nu}=\frac{1}{\lambda}\text{ cm}^{-1}$$

W. Ritz (1908) suggested that the frequency of any line in a particular spectral series of a given atom can be represented as a difference of two terms, one of which is constant and other variable throughout the series. This is known as Ritz combination principle. Mathematically we can write,

$$\bar{\nu}=\frac{1}{\lambda}=R\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) \quad \ldots (20.3)$$

where n_1 and n_2 are integers ($n_1>n_2$) and R is the Rydberg's constant for hydrogen. For a particular series, the integer n_2 remains constant throughout but n_1 varies from one line to another. Five different series of lines have been observed experimentally. These are:

(*a*) **Lyman series.** When an electron jumps from any outer orbit to the first orbit, this series originates and it lies in the ultraviolet region of the spectrum. Here $n_2=1$ and $n_1=2, 3, 4, 5, \ldots$. The relation (20.3) can be written as

$$\bar{\nu}=\frac{1}{\lambda}=R\left(\frac{1}{1^2}-\frac{1}{n_1^2}\right) \quad \ldots (20.4)$$

This series was predicted by Bohr and was photographed by T. Lyman.

(*b*) **Balmer series**. This series lies in the visible region and occurs when an electron jumps from an outer orbit to the second orbit *i.e.*, $n_2=2$ and $n_1=3, 4, 5, \ldots$ The relation (20 3) thus modifies to

$$\bar{\nu}=\frac{1}{\lambda}=R\left(\frac{1}{2^2}-\frac{1}{n_1^2}\right) \quad \ldots (20.5)$$

The wavelengths were found to be 1215.05, 972.54, 950.00 and 935.0 Å.

(*c*) **Paschen series**. This series falls in the infra-red region and originates when an electron jumps from an outer orbit to the 3rd orbit, *i e.*, $n_2=3$ and $n_1=4, 5, 6, \ldots$ The relation (20.3) takes the form

$$\bar{\nu}=\frac{1}{\lambda}=R\left(\frac{1}{3^2}-\frac{1}{n_1^2}\right) \quad \ldots (20.6)$$

(*d*) **Bracket series**. This series also falls in the infra-red region and results when an electron jumps from an outer orbit to the 4th orbit, *i e.*, $n_2=4$ and $n_1=5, 6, 7, \ldots$ The relation (20.3) becomes

$$\bar{\nu}=\frac{1}{\lambda}=R\left(\frac{1}{4^2}-\frac{1}{n_1^2}\right) \quad \ldots (20.7)$$

(*e*) **Pfund series**. This again lies in the infra-red region and originates when an electron jumps from some outer orbit to the 5th orbit *i.e.*, $n_2=5$ and $n_1=6, 7, 8, \ldots$ The relation (20.3) takes the form:

$$\bar{\nu}=\frac{1}{\lambda}=R\left(\frac{1}{5^2}-\frac{1}{n_1^2}\right) \qquad \ldots (20.8)$$

At the time of development of the Bohr theory only Balmer and Paschen series were known. Rest of the series were predicted by Bohr and were observed much later. When an electron jumps from an higher energy level to a lower energy level, it emits radiations giving rise to the emission spectra. On the other hand when an electron jumps from an orbit of lower energy to an orbit of higher energy it gives rise to the absorption spectra. The five series of lines of the atomic hydrogen are shown in Fig. 20.9 and Fig. 20.10.

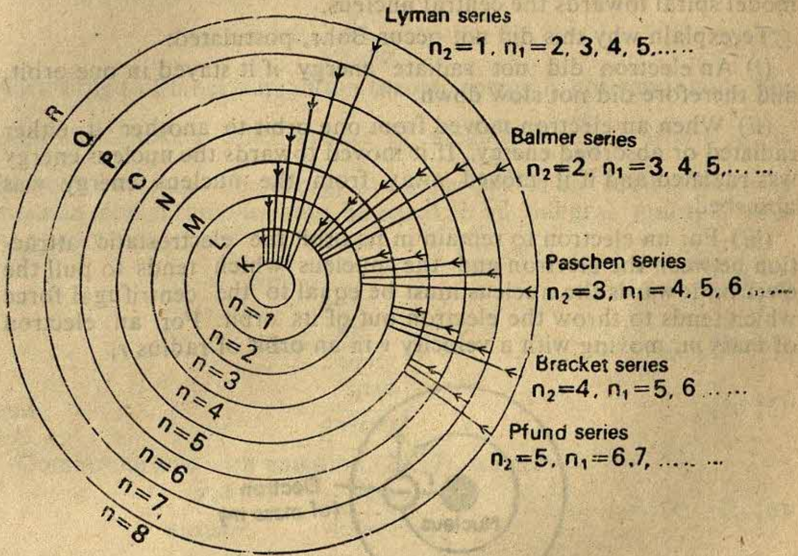

Lyman series
$n_2=1,\ n_1=2, 3, 4, 5, \ldots$
Balmer series
$n_2=2,\ n_1=3, 4, 5, \ldots$
Paschen series
$n_2=3,\ n_1=4, 5, 6 \ldots$
Bracket series
$n_2=4,\ n_1=5, 6 \ldots$
Pfund series
$n_2=5,\ n_1=6, 7, \ldots$
R
Q
P
O
N
M
L
K
n=1
n=2
n=3
n=4
n=5
n=6
n=7
n=8

Fig. 20.8. Diagrammatic representation of the origin of hydrogen spectrum.

	Region of Spectrum
Lyman Series	Ultraviolet
Balmer Series	Visible/ultraviolet
Paschen Series	Infra-red
Brackett Series	Infra-red
Pfund Series	Infra-red.

20.10. BOHR MODEL OF ATOM

Niel's Bohr a young Danish physicist was working with Ernest Rutherford on the theoretical aspects of atomic structure. He was highly impressed by Rutherford's new atomic model in which electrons revolved around the nucleus located at the centre. He could not understand the analogy between the Rutherford model and the movement of the planets around the sun, because the planets are electrically neutral while the electrons are heavily charged with negative electricity. From the theory of electricity we know that revolving electric charge always emits electromagnetic waves. The emission of electromagnetic waves must result in the loss of energy by the emitting particle and this led the electrons in the Rutherford model spiral towards the central nucleus.

To explain why this did not occur Bohr, postulated:

(*i*) An electron did not radiate energy if it stayed in one orbit, and therefore did not slow down.

(*ii*) When an electron moved from one orbit to another it either radiated or absorbed energy. If it moved towards the nucleus energy was radiated and if it moved away from the nucleus energy was absorbed.

(*iii*) For an electron to remain in its orbit the electrostatic attraction between the electron and the nucleus which tends to pull the electron towards the nucleus must be equal to the centrifugal force which tends to throw the electron out of its orbit. For an electron of mass *m*, moving with a velocity *v* in an orbit of radius *r*,

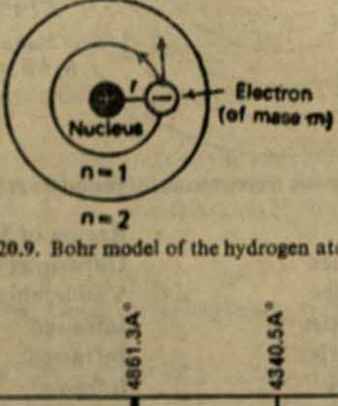


Fig. 20.9. Bohr model of the hydrogen atom.

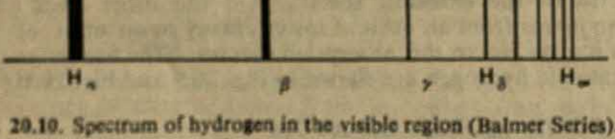


Fig. 20.10. Spectrum of hydrogen in the visible region (Balmer Series).

$$\text{Centrifugal force} = \frac{mv^2}{r} \qquad \ldots (20.9)$$

If the charge on the electron is *e*, the number of charges on the nucleus *Z*, the permittivity of vacuum, ϵ_0

The coulombic force of attraction $= \dfrac{Ze^2}{4\pi\epsilon_0 r^2}$ ... (20.10)

At equilibrium, we have

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 mr^2} \quad \text{... (20.11)}$$

From relation (20.11), we get

$$v^2 = \frac{Ze^2}{4\pi\epsilon_0 mr} \quad \text{... (20.12)}$$

According to Planck's quantum theory, energy is not continuous but occurs in 'Packets' called quanta of magnitude $\frac{h}{2\pi}$, where h is Planck's constant. The energy of an electron in an orbit that is its angular momentum mvr must be equal to an integral multiple of n of quanta *i.e.*,

$$mvr = \frac{nh}{2\pi} \quad \text{... (20.13)}$$

$$\therefore \quad v = \frac{nh}{2\pi mr} \quad \text{... (20.14)}$$

$$\text{and} \quad v^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \quad \text{... (20.15)}$$

Combining this with equation (20.12), we get

$$\frac{Ze^2}{4\pi\epsilon_0 mr} = \frac{n^2h^2}{4\pi^2m^2r^2} \quad \text{... (20.16)}$$

hence

$$r = \frac{\epsilon_0 n^2h^2}{\pi me^2Z} \quad \text{... (20.17)}$$

For hydrogen $Z=1$ and if

$n=1$ $r=1^2\times0.0529$ nm

$n=2$ $r=2^2\times0.0529$ nm

$n=3$ $r=3^2\times0.0529$ nm

This gives a picture of the hydrogen atom where an electron moves in circular orbits of radius proportional to $1^2, 2^2, 3^2, \ldots$ and radiates energy only when the electron jumps from one orbit to another.

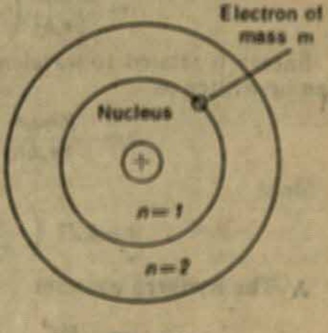


Fig. 20.11.

Calculation of energy. We begin by defining the energy of the system. The total energy is the sum of the electron's kinetic energy and its potential energy in the field of the nucleus. Let m be the mass of the electron and v its velocity, r is its distance from the nucleus. The kinetic energy is simply $\frac{1}{2}mv^2$, while the potential energy, is some function of r. The potential energy of a particle is a function of its position and the forces acting on it It is strictly defined only for conservative systems, those system with no frictional or other dissipative forces. If in such a system a particle moves from point ∞ to r the potential energy is given by,

$$V(r)-V(\infty)=\int_r^{\infty} F(r)dr=\frac{q_1\, q_2}{4\pi\epsilon_o}\int_r^{\infty}\frac{dr}{r^2} \qquad \ldots (20.18)$$

The zero of potential energy can be set arbitrarily and it is convenient to set it at $V(\infty)=0$. For atomic systems under consideration $q_1=+Ze$, $q_2=-e$ $V(r)=-Ze^2/4\pi\epsilon_o r$. The total energy, E_T is

$$E_T=\frac{mv}{2}-\frac{Ze^2}{4\pi\epsilon_o\, r} \qquad \ldots (20.19)$$

From relation (20.12) $\frac{mv^2}{2}=\left(\frac{Ze^2}{4\pi\varepsilon_o\, r}\right)=\frac{Ze^2}{8\pi\epsilon_o\, r}$ ... (20.20)

On substituting this value in (20.19) we get

$$E_T=\frac{Ze}{8\pi\epsilon_o\, r}-\frac{Ze}{4\pi\epsilon_o\, r}=-\frac{Ze^2}{8\pi\epsilon_o r}. \qquad \ldots (20.21)$$

The energy of any stable orbit is of course negative, approaching the limit E_o as n becomes infinite. The absolute value of energy is proportional to the mass and to the square of the nuclear charge.

If an electron jumps from an orbit 1 to a orbit Z, the change in energy $\triangle E$ is given by the relation

$$\triangle E=\left(-\frac{Z^2e^4m}{8\epsilon_o n^2{}_1h^2}\right)-\left(\frac{Z^2e^4m}{8\epsilon_o n^2{}_2h^2}\right) \qquad \ldots (20.22)$$

$$=\frac{Z^2me^4}{8\epsilon_o h^2}\left(\frac{1}{n^2{}_2}-\frac{1}{n_1{}^2}\right) \qquad \ldots (20.23)$$

Energy is related to wavelength ($E=hc\bar{\nu}$) then equation (20.23) can be written as

$$\bar{\nu}=\frac{Z^2me^4}{8\epsilon_o h^3c}\left(\frac{1}{n^2{}_2}-\frac{1}{n^2{}_1}\right)$$

Since

$$\bar{\nu}=RZ^2\left(\frac{1}{n_2{}^2}-\frac{1}{n_1{}^2}\right) \qquad \ldots (20.24)$$

♣ The Rydberg constant

$$R=\frac{me^4}{8\epsilon_o h^3c} \qquad \ldots (20.25)$$

The experimental value of R is 1.097373×10^{-7} m^{-1}, in good agreement with the theoretical value of 1.096776×10^{7} m^{-1}. The Bohr theory provides an explanation of the atomic spectra of hydrogen. The different series of spectral lines can be obtained by varying the values of n_1 and n_2 in equation (20.24). Thus with $n_2=1$, $n_1=2, 3, 4 \ldots$ we obtain the Lyman series of line in the *UV* region. With $n_2=2$, $n_1=3, 4, 5, \ldots$ we get Balmer series of lines in the visible spectrum. Similarly, $n_2=3$, $n_1=4, 5, 6 \ldots$ gives the Paschen series $n_2=4$, $n_1=5, 6, 7 \ldots$ the Brackett series, and $n_2=5$, $n_3=6, 7, 8 \ldots$ gives the *P*fund series. The various transitions possible are shown in Fig. 20.12.

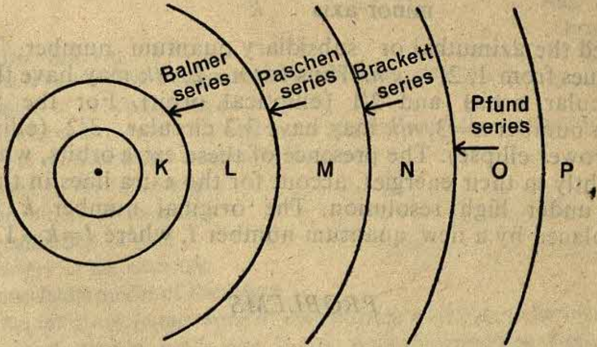


Fig. 20.12. Bohr Orbits of hydrogen and various series of spectral lines.

Refinements of the Bohr Theory

It has been assumed that the nucleus remains stationary except for rotating on its own axis. This would be true if the mass of the nucleus were infinite, but the ratio of the mass of an electron to the mass of the hydrogen nucleus is 1/1836. The nucleus actually oscillates slightly about the centre of gravity, and to allow for this the mass of the electron m is replaced by the reduced mass μ *i.e.*

$$\mu=\frac{mM}{m+M} \qquad \ldots (20.26)$$

where M is the mass of the nucleus. The inclusion of the mass of the nucleus explains why different isotopes of an element produce lines in the spectrum at slightly different wave numbers.

The orbits are sometimes denoted by letters *K*, *L*, *M*, *N*, counting outwards from the nucleus, and these are also numbered, 1, 2, 3, 4 . . . This number is called the principal quantum number, which is denoted by the symbol n. It is therefore possible to define which circular orbit is under consideration by specifying the principal quantum number.

The movement of an electron from one orbit to another should give a single sharp line in the spectrum, corresponding precisely to the energy difference between the initial and final orbits. If the hydrogen spectrum is observed with a high resolution spectrometer some of the lines show fine structure *i.e.* they are composed of more than one line close together. This was explained by Sommerfeld in terms of elliptical orbits which precessed in space round the nucleus For the value of $n=1$ there is a circular orbit but for $n=2$ both circular and elliptical orbits are possible. To define an elliptical orbit, a second quantum number k is needed. The shape of the ellipse is defined by the ratio of the lengths of the major and minor axis. Thus

$$\frac{\text{major axis}}{\text{minor axis}}=\frac{n}{k}$$

k is called the azimuthal or subsidiary quantum number. This may have values from 1, 2, . . . n. Thus for $n=2$, n/k may have the values 2/2 (circular orbit) and 2/1 (elliptical orbit). For the principal quantum number $n=3$, n/k may have 3/3 circular, 3/2 (ellipse) and 3/1 (narrower ellipse). The presence of these extra orbits, which differ only slightly in their energies, accout for the extra lines in the spectra revealed under high resolution. The original number k has now been replaced by a new quantum number l, where $l=k-1$.

PROBLEMS

1. What are Cathode Rays? Give an account of their properties.

2. What is meant by the term "model"? Discuss Rutherford's model of the atom. What are its defects?

3. What is meant by the term "stationary state"? Discuss Bohr's atomic model.

4. Calculate energy of the hydrogen atom using Bohr's theory.

In the emission spectrum of hydrogen, the spectral series with n equal to three is called the Paschen series and is observed in the infrared region of the spectrum. Calculate the wave number for this series of lines.

Ans. 1.22×10^4 cm^{-1}

5. Consider an excited hydrogen atom with an electron in the $n=4$ energy level. What transitions are possible for this atom to reach the ground state ($n=1$)? Draw a diagram to explain it.

6. (*a*) Calculate the value of Rydberg's constant R and compare it with the experimentally determined value.

(*b*) Calculate the radii for the Bohr's orbit with $n=1$ and $n=2$.

Ans. 0529 Å; 2.166 Å

7. What is meant by Atomic number of an element? How is it determined? Discuss the statement that "Atomic number of an element is more fundamental than atomic weight." What is the importance of this statement?

8. Derive an expression for the energy levels of the earth around the sun, using the Bohr-theory. What approximately is the quantum number corresponding to the present state of motion of the earth? The unusual gravitational constant is $6\ 670\times10^{-8}$ cm^{-3} g^{-1} sec^{+2}. the mass of the earth is 5.983×10^{24} kg and the mass of the sun is 3.2939×10^5 times the mass of the earth.

9. (*a*) Discuss Millikan's method for the determination of charge of an electron.

(*b*) In the Millikan oil drop experiment the following data were obtained: distance between plates, 1 60 cm; voltage 4550/300; density of air 1.2×10^{-3} g/cm^3; distance of fall 0.60 cm; viscosity of the air 1.824×10^{-4} g cm^{-1} sec^{-1}; density of oil 0.90 g/cm^3; average time of fall 21.2 sec; successive times of rise 46.2, 27.8, 15.7, 13.0, 45.0 and 21.2 sec; (*a*) calculate the radius of the oil drop, (*b*) calculate the average charge on the electron and compare it with the accepted value.

Ans. (*a*) $r=1.62\times10^{4}$ cm;
$m=1.60\times10^{-11}$ g:
(*b*) 4.84×10^{-10} e.s.u.

10. The wavelength of the K_{α} characteristic X-rays of iron and potassium are 1.931×10^{-8} and 3.737×10^{-8} cm respectively. What is the atomic number and the name of the element for which the characteristic K_{α} wavelength is 2.289×10^{-8} cm ? (The velocity of light is 3×10^{10} cm/sec).

Ans. $Z=24$
chromium

11. Explain the following:
    (*a*) There is no electric charge on the atom of an element;
    (*b*) The sign of the charge on an electron;
    (*c*) The difference between a continuous spectrum and line spectrum;
    (*d*) Atomic number of an element.
12. Write notes on the following:
    (*a*) Composition of nucleus;
    (*b*) Determination of *e*/*m*;
    (*c*) Discovery of the electron;
    (*d*) Sommerfeld's model of the Atom.
13. Explain the following in the terms of the structure of the particles involved.
    (*a*) A beam of cathode rays is bent in the opposite direction from that of a beam of positive rays when both go through a magnetic field.
    (*b*) All the particles in every beam of cathode rays have the same mass.
    (*c*) The particles in different beams of positive rays may have different masses.

Chapter 21

WAVE MECHANICAL MODEL OF THE ATOM

21.1. INTRODUCTION

Light moves without dragging the medium through which it travels. This kind of movement is referred to as a travelling wave. We can say that waves can propagate through a material medium. Here it may be noted as to how water moves more rapidly along causing the water to move up and down, but the water itself moves little more than that. The wave front moves forward, but place a cork on the water or watch a boat bobbing on the waves and see how little their forward motion is. However, whereas sound moves in waves and see how little their forward motion is. However, whereas sound waves move in through the medium of the air and wave fronts propagate through water medium, light spreads out in waves and moves through empty space. What medium is supporting its vibration ? Presumably none. That caused a lot of trouble among scientists for a long time after all, how were they to explain moving through nothing ? "It was a hard pill for the scientists to swallow. Therefore scientists at first created the "ether" a medium for light to travel through, They just could not accept that something was moving through nothing. But the theory wore in thin in the last years of the nineteenth century and mostly collapsed on evidence from experiment of Michelson—Morley ether drift experiment which demonstrated that we really can not tell whether we are in motion or at rest with respect to this "ether" medium. Think about rowing a boat upstream, you have to overcome the resistance due to the drift of the river (the medium). The same is true when moving through air. But this mysterious ether medium did not drift. Light was not slowed by passage through this medium, perhaps the best conclusion to draw was simply that no "ether" medium existed.

The quantum concept dominated the development of atomic and molecular physics in the early part of this century. A catastrophic situation arose when three very different phenomena, all inexplicable within the framework of classical physics. could be explained from the concept of the quantum of action. These phenomena are

(*i*) Black-body radiation

(*ii*) Photo electric effect

(*iii*) Bohr theory for the spectrum of Hydrogen.

21.2. BLACK BODY RADIATION

In this section, we shall discuss the black-body radiation. Imagine a solid object with a hollow interior and its exterior is completely insulated from the outside world. On heating to 700—800°C, it should glow bright orange. The black-body glows only in its own interior and can not lose any energy to the outside world, it will soon reach a state of thermal equilibrium, when it will require no additional energy from the heating wires to maintain a constant temperature. But those inside walls are still radiating. Will the solid object lose all its energy to the cavity simply by emission of radiation? Clearly it will not, as some of that radiation must be reabsorbed by the walls. As soon as the steady temperature is reached, no net energy enters the cavity. Every small bit of energy that appears as radiation must be paid for by an equal amount of radiation energy absorbed by the walls. This is known as black body. The classical problem, the very first problem to involve the concept of quantum was this; How much energy is present as radiation in a given volume of "empty space" within such a simple hot object held at any definite temperature ? Another related question could be, "what is the distribution of the energy in the cavity, as a function of the wavelength? For example is the radiation all of the same frequency? A simple experiment tells us that it is not so. The behaviour of the black body radiation is shown in Fig. 21.1.

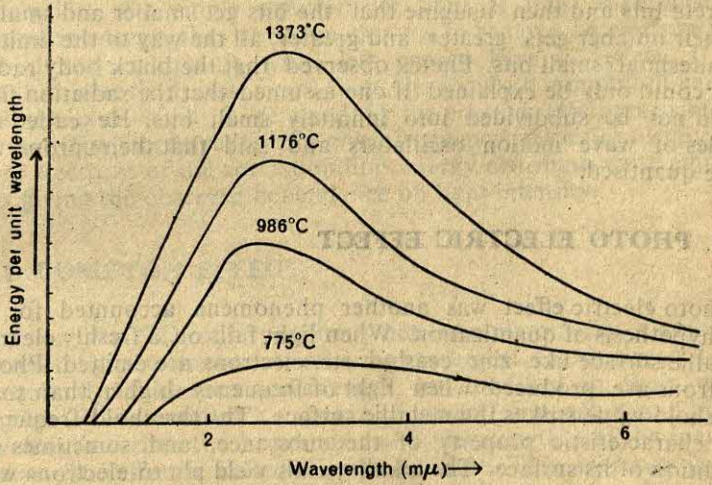


Fig. 21.1. Energy distribution of a black body radiation.

As shown in Fig. 21.1, the radiation intensity gives a broad smooth distribution that varies with the temperature of the black body. This is quite similar to the radiation given off by any hot object. What one would like to know is why the energy distribution of black-body has this particular form. Rayleigh & Jeans made a great stride towards the solution of the black body problem, he suggested that one thinks of the radiation within the black body as standing waves forced to remain in the cavity by the condition that there be no wave displacement in any direction at the boundary walls. These waves are analogous to the vibration in a jump rope or a violin string whose ends are kept in tight condition, so that they cannot be displaced.

Rayleigh and Jeans computed how many modes of wave motion can be contained in a given cavity and satisfy the stated boundary condition, they found that the number of modes should increase steadily with frequency, becoming infinite in the short-wavelength limit. According to the classical theory, applied by Rayleigh and Jeans, the radiation energy should be distributed evenly over all these modes and thus an infinite amount of energy should be stored in short wavelength modes. By contrast, the experimental data show that the energy distribution drops sharply at short-wavelength. Thus the theory only gives a satisfactory description of the long wavelength end of the spectrum but was not successful in short-wavelength region. This led to what was known as ultraviolet catastrophe.

This problem was successfully resolved by Plank. Classically one assumed that the energy distribution could be carried out by a method like that used to define a derivative or an integral. According to Planck, one begins by chopping a system into small but discrete bits and then imagine that the bits get smaller and smaller as their number gets greater and greater, all the way to the limit of infinitesimal small bits. Planck observed that the black body radiation could only be explained if one assumed that the radiation field could not be subdivided into infinitely small bits. He called the modes of wave motion oscillators and said that their properties were quantised.

21.3. PHOTO ELECTRIC EFFECT

Photo electric effect was another phenomena accounted for by the hypothesis of quantization. When light falls on a freshly cleaned metallic surface like zinc, ceasium etc, electrons are emitted. Photoelectrons are produced when light of frequency higher than some threshold value strikes the metallic surface. The threshold frequency is a characteristic property of the substance, and sometimes the condition of its surface. The alkali metals yield photo-electrons with visible light, but for most substances the threshold lies in the ultraviolet.

The rate of electron emission can be determined by measuring the current through a collector plate, the electrons kinetic energy is measured by the voltage required to prevent them from reaching the collector. Below the threshold frequency ν_0, no electrons are at all emitted. Above ν_0, electrons with different energies are obtained; the energy distribution is independent of the light intensity but varies with frequency. The maximum electron energy for a frequency ν obeys the equation

$$E_{max}=h\nu-h\nu_0 \qquad \ldots (21.1)$$

where h is Plank's constant; $h\nu_0$ is known as work function. For a given frequency, the rate of electron emission is proportional to the light intensity.

These results were puzzling in terms of the wave theory of light. Since the energy delivered by a wave increases the wave's amplitude, one would thus expect the energy of emitted electrons to increase with the light intensity.

However, if the energy were distributed uniformly, it would take rather a larger time for any one electron to obtain the observed energy, but no such lag is observed. This can be explained if we assume that light can behave both as a stream of particles and as wave. This explanation was given by Einstein in 1905. He assumed that the light striking a photoelectric surface consists of discrete particles or quanta each having a definite energy proportional to the frequency of the light, $E=h\nu$.

Each electron emitted from the surface then corresponds to the absorption of a single quantum of light. It must take a certain minimum energy, the work function $h\nu_0$ to remove an electron from a solid surface; quanta with less energy have no effect. If the quantum absorbed has more than the requisite amount of energy, then the extra energy is retained by the emitted electrons as kinetic energy. The more quanta of a given frequency strike the surface, the more electrons of the corresponding energy distribution are emitted, thus giving the observed dependance on light intensity.

21.4. COMPTON EFFECT

Compton, in 1922, observed that when monochromatic X-rays are scattered by carbon or some other light element, the scattered X-rays are not only of the same wave-length, but modified in their wavelengths. These modified X-rays are of lower frequency ν' and higher wavelength λ' than the frequency ν and wavelength λ of the incident X-rays. The effect is called Compton effect. This increase in the wave-length of X-rays after scattering from the surface of an object is due to the decrease in energy, by the interaction between X-rays and electrons.

In the Fig. 21.2, $h\nu$ is energy of photon striking the surface M and $h\nu'$ is energy of the scattered photon. Let λ and λ' be the corresponding wave lengths to these frequencies *i.e.*, ν and ν'.

Compton found that $d\lambda$ the difference in wave lengths $(\lambda'-\lambda)$ could be given by the equation,

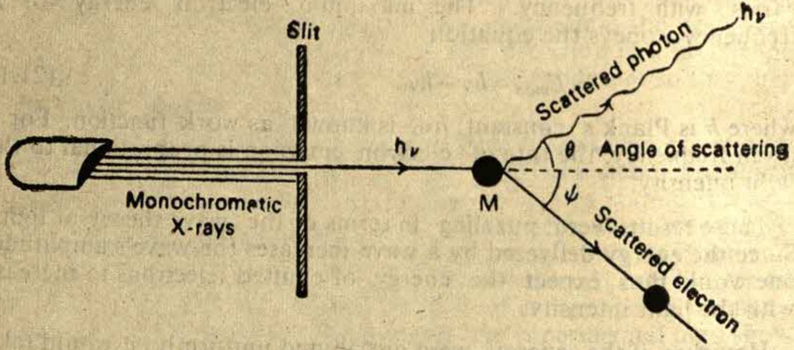


Fig. 21.2. Scattering of X-rays.

$$d\lambda=\frac{2h}{mc}\sin^2\theta/2 \qquad \ldots (21.2)$$

where m is the mass of the electron, c the velocity of light and θ is the angle of scattering. The above equation clearly shows that $d\lambda$ is independent of the incident wavelength *i.e.* λ and nature of the substance.

21.5. DE BROGLIE'S CONCEPT OF MATTER WAVES

According to de Broglie, the two fundamental forms, matter and energy, in which nature manifests herself, must mutually be symmetrical. Since the radiant energy has been shown to possess a dual nature—wave and particle, matter must also possess the same dual nature *i.e.* particle and wave. It was for this that de Broglie was awarded Noble Prize in 1929. He stated that there is an intimate relation between waves and corpuscles not only in case of radiation but also in case of matter. He gave the following relation between the wave and particle nature of electron,

$$\lambda=\frac{h}{mv} \qquad \ldots (21.3)$$

where m is the mass of the electron moving with a velocity v and λ is the wave length of the light emitted. Thus, in de Broglie model of atom, an electron exists as a standing wave in each orbit. It may be noted that an orbit can contain a wave which is full and hence in accordance with Bohr's postulate. Mathematically, the length of an orbit whose radius is r, is given by $2\pi r$ and $2\pi r=n\lambda$ where n is an integer.

Since $\lambda=\dfrac{h}{mv}$

We have, $2\pi r=\dfrac{nh}{mv}$ ...(21.4)

or $mvr=n.h/2\pi$ ...(21.5)

This is Bohr's postulate of quantisation. It is one of the success of this model that led to the development of electron microscope.

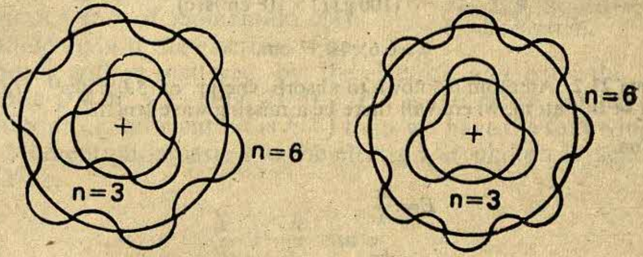


Fig. 21.3. de Broglie's waves.

de Broglie equation was verified experimentally by Davisson and Germer by their electron diffraction experiment. It is possible to accelerate or retard electrons, that is, to alter their momentum, by making them pass through an electric field. If the momentum is doubled, the wavelength must fall to half and the interference rings must likewise shrink to half their size. From the size of the rings we can conclude the wavelength of the electrons is of the same order of magnitude as that of X-rays. This is shown in Fig. 21.3.

G.P. Thomson's experiment. An accelerated pencil beam of electrons, when made to pass through a fine hole gave concentric rings on a photographic film. Pattern of photograph and apparatus used is shown in Fig. 21.4.

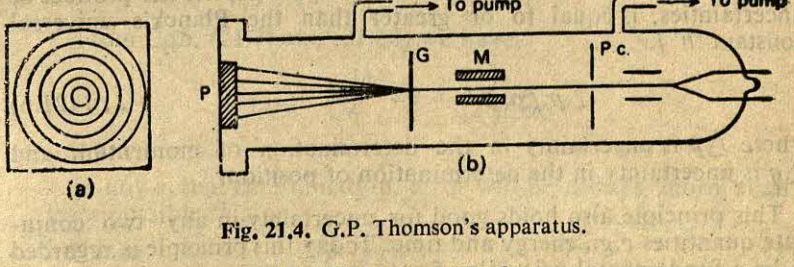


Fig. 21.4. G.P. Thomson's apparatus.

P=Photographic film
G=Thin Gold foil (10^{-6} cm)
M=Metal block to mkae a pencil beam
$P.C.$=Perforated cathode to accelarate the beam

It was also found that the radii of rings decrease with the increase in velocity of the electrons as is expected from De Broglie relation.

Problem 21.1. What is the wave length of a ball of mass 100 g moving with a velocity of 1.0×10^2 cm/sec?

Solution

$$\lambda = \frac{h}{mv}$$

$$= \frac{(6.63 \times 10^{-27} \text{ erg-sec})}{(100 \text{ g})\ (1 \times 10^2 \text{ cm/sec})}$$

$$\lambda = 6.6 \times 10^{-31} \text{ cm.}$$

Problem 21.2. An atom is known to absorb energy of 5.0×10^{-11} erg. In the spectrum of this atom, where will there be a missing wave length?

Solution.

$$E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E}$$

$$= \frac{6.63 \times 10^{-27} \text{ erg-sec} \times 3.0 \times 10^{10} \text{ cm} \times 1 \text{ Å}}{5.0 \times 10^{-11} \text{erg-sec} \times 10^{-8} \text{ cm}}$$

$$= 400 \text{Å}$$

21.6. HEISENBERG'S UNCERTAINTY PRINCIPLE

Quantum mechanics shows us that the position of a particle and its momentum can be known only, within certain limits, which are of great significance in the submicroscopic world of atoms and atomic particles.

The uncertainty principle states that in simultaneous determination of the position and momentum of a particle, *i.e.* the product of uncertainties, is equal to or greater than the Planck's universal constant '*h*' *i.e.*,

$$\triangle p . \triangle q \geqslant h \qquad \ldots (21.6)$$

where $\triangle p$ is uncertainty in the determination of momentum and $\triangle q$ is uncertainty in the determination of position.

This principle also holds good for uncertainty in any two conjugate quantities *e.g.*, energy and time. Today this principle is regarded to be a fundamental principle of nature.

To explain the principle mathematically, we proceed as under:

Let an electron at position O be observed with the help of a X-ray microscope whose resolving power is given by

$$\triangle q=\frac{\lambda'}{2\sin\alpha} \quad \ldots (21.7)$$

where $\triangle q$ is uncertainty in the determination of position of electron and λ' is wavelength of photon entering the microscope at an angle α.

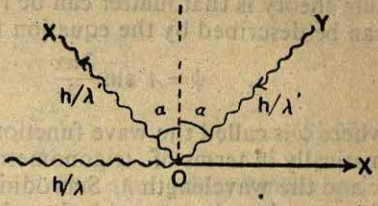


Fig. 21.5. Scattering of light by the electron.

Now let a photon of wavelength λ (*i e.* of momentum h/λ) collide against the electron. The photon will be scattered by the electron and enter the microscope along *OX* or *OY* (Fig. 21 5). If λ' is the wave length of scattered photon (*i.e.* momentum is h/λ') than we have the following equations:

Momentum imparted to the electron, if photon is scattered along *OX i.e.*

$$\frac{h}{\lambda}+\frac{h}{\lambda'}\sin\alpha \quad \ldots (21.8)$$

Momentum imparted to the electron if photon is scattered along *OY* is given by

$$\frac{h}{\lambda}-\frac{h}{\lambda'}\sin\alpha \quad \ldots (21.9)$$

From equations (21.6) and (21.7), it is clear that the momentum imparted to electron can have any value in between the two values give byn equation (21.8) and equation (21.9).

Hence the uncertainty in momentum is given by

$$\triangle p=\left(\frac{h}{\lambda}+\frac{h}{\lambda'}\sin\alpha\right)-\left(\frac{h}{\lambda}-\frac{h}{\lambda'}\sin\alpha\right)$$

$$=\frac{2h}{\lambda'}\sin\alpha \quad \ldots (21.10)$$

From Eqn. (21.7) and (21.10) we have,

$$\triangle p.\triangle q=\frac{2h}{\lambda'}\sin\alpha.\ \frac{\lambda'}{2\sin\alpha}$$

$$=h$$

In any actual determination, error will be always more than the least possible '*h*'.

Hence $\triangle p.\triangle q \geqslant h$ ... (21.11)

21.7. SCHRÖDINGER'S WAVE EQUATION

Schrödinger used de Broglie's idea of matter waves and developed it into rigorous mathematical theory. The relation of de Broglie is fused into the classical wave equation. The basic idea of quantum theory is that matter can be regarded as wave and these waves can be described by the equation for a vibrating string, *i.e.*,

$$\psi = A \sin\frac{2\pi x}{\lambda} \qquad \ldots (21.12)$$

where ψ is called the wave function, and can be described mathematically in terms of trigonometric sine function of displacement x and the wavelength λ. Schrödinger assigned this sine wave equation to the electron with the object of describing the behaviour of the electron in terms of its kinetic energy and potential energy.

Differentiating equation (21.12) we get,

$$\frac{d\psi}{dx} = \frac{2\pi A}{\lambda} \cos \frac{2\pi x}{\lambda} \qquad \ldots (21.13)$$

Differentiating equation (21.13) second time, w.r.t. x,

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2 A}{\lambda^2} \sin \frac{2\pi x}{\lambda} \qquad \ldots (21.14)$$

Since $\psi = A \sin \frac{2\pi x}{\lambda}$

Relation (21.14) can be written as

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi \qquad \ldots (21.15)$$

Kinetic energy of a particle of mass m, moving with a velocity v is given by

$$\text{K.E.} = \tfrac{1}{2} mv^2 \qquad \ldots (27.16)$$

where m is its mass and v the velocity. On multiplying and dividing right hand side of equation (21.16) by m

$$\text{K.E.} = \tfrac{1}{2}\frac{m^2v^2}{m} \qquad \ldots (21.17)$$

de Broglie equation can be expressed as,

$$mv = \frac{h}{\lambda} \qquad \ldots (21.18)$$

On squaring both sides of equation (21.18)

$$m^2v^2 = \frac{h^2}{\lambda^2} \qquad \ldots (21.19)$$

On comparing equations (21.17) and (21.19) we get

$$\text{K.E.} = \frac{1}{2m}\frac{h^2}{\lambda^2} \qquad \ldots (21.20)$$

From equation (21.15)

$$\lambda^2 = -\frac{4\pi^2\psi}{\dfrac{d^2\psi}{dx^2}} \qquad \ldots (21.21)$$

On substituting the value of λ^2 from equation (21.21) in equation (21.20).

$$\text{K.E.} = -\frac{1}{2m}\,\frac{h^2}{4\pi^2\psi}\cdot\frac{d^2\psi}{dx^2}$$

$$= -\frac{h^2}{8\pi^2 m\psi}\cdot\frac{d^2\psi}{dx} \qquad \ldots (21.22)$$

The total energy E, of a particle is the sum of its kinetic and potential energy. Thus,

$$\text{K.E.} = (E-V) = \frac{h^2}{8\pi^2 m\psi}\;\frac{d^2\psi}{dx^2} \qquad \ldots (21.23)$$

Rearrangement of this gives,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \qquad \ldots (21.24)$$

This is Schrödinger equation in one dimension. While dealing with atomic structure, it is expanded to three dimensions using the cartesian coordinates, x, y, z. Equation (21.24) can be written in the form

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \qquad \ldots (21.25)$$

where ψ is called the wave function or the probability amplitude function, E is the total energy of the system which is constant for a given value of λ, V is potential energy which depends upon the position of the system. Since E is constant and V is variable, therefore $(E-V)$ is also a variable. The wave equation is a differential equation of second order.

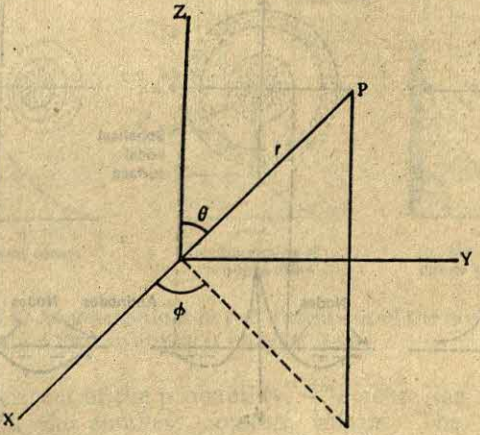


Fig. 21.6. Polar coordinates.

The Schrödinger's equation can be expressed in polar coordinates r, θ and ϕ, where r is the radial distance of a point from the origin, θ is the inclination of the radial line to the Z-axis and ψ is the angle made with the X-axis by projecting the radial line in the $X-Y$ plane. [See Fig. (21.6)].

The solutions for ψ are called wave functions and may be expressed as the product of three functions each of which depends only on one of the coordinates.

$$\psi(r, \theta, \phi)=R(r)\Theta(\theta)\Phi(\phi) \qquad \ldots (21.26)$$

where $R(r)$ is a function that depends on the distance of the electron from the nucleus, which in turn depends on the quantum numbers n and l.

$\Theta(\theta)$ is a function of θ, which depends on the quantum numbers l and m. $\Phi(\varphi)$ is a function of φ which depends on the quantum number m.

21.8. NATURE OF THE WAVE FUNCTION

The wave function ψ is a sort of amplitude function. It is not an observable quantity but $|\psi\psi^*|$ is observable where ψ^* is the conjugate of ψ. If the function is equal to its conjugate than ψ^2 gives the probability of finding the electron within a given volume.

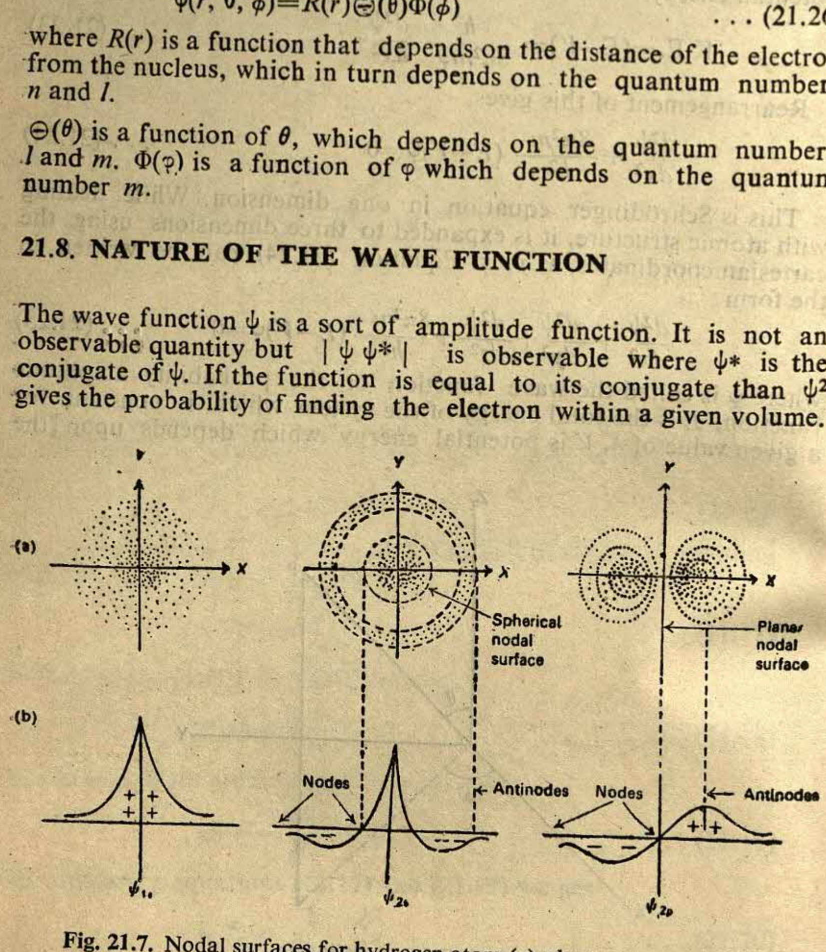


Fig. 21.7. Nodal surfaces for hydrogen atom (*a*) electron probability density (*b*) Electron wave functions (+ and − signs denote phase).

Where ψ^2 is high, the probability of finding the electron is high. Where ψ^2 is low, the electron is rarely found. The information contained in ψ^2 can be likened on the information contained in the holes in a *dart* board. The pattern of holes shows that there is a high probability that the dart will land within a circle containing many dart holes and a low probability for a circle of equal area but containing few dart holes. The density of dart holes gives probability information. Figure 21.7 shows the ways in which the probability distribution for a hydrogen 1*s* wave function can be represented in two dimensions. Figure 21.8 (*i*) represents the density of such dots as a function of position on a dart board. This picture gives a qualitative picture of where the electron is most likely to be found. Figure 21.8 (*ii*) shows the graph of dot density ψ^2 as a function of r, the distance from the nucleus.

Fig. 21.8 (*iii*) represents the density contours on a cross-sectional through a probability dot diagram of Fig. 21.8 (*a*). The significance of such density contours is shown in Fig. 21.8 (*iv*). It represents a contour map of where the electron spends its time. Such a map depicts qualitatively the shape of distribution and it displays quantitatively, how rapidly the probability falls from the nucleus. Figs. 21.8 (*v*) and (*vi*) represent the density sum and the significance of the density sum. The inner most contour line is the line that encloses 10 per cent of the probability. The next line that encloses 50 per cent in the smallest possible volume. The third contour shows the 90 per cent enclosure line. These contours are very useful as they tell us where the electron is most likely to be found and also about the size of the atom.

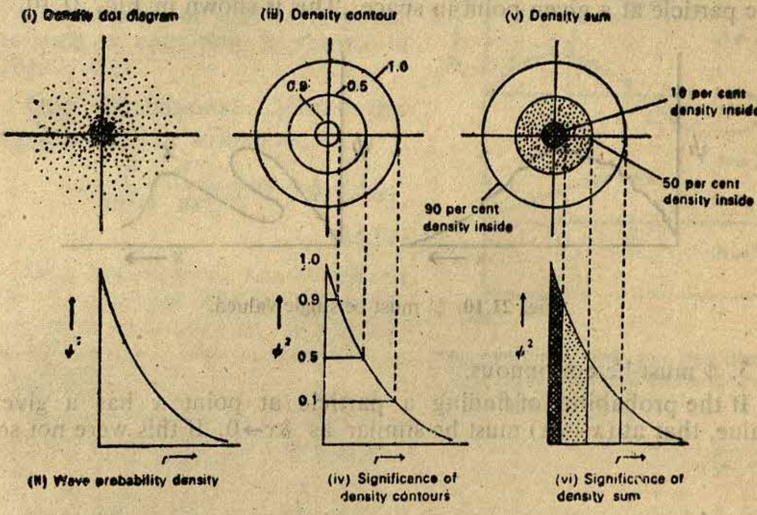

(i) Density dot diagram
(iii) Density contour
(v) Density sum
1.0
0.9
0.5
10 per cent density inside
50 per cent density inside
90 per cent density inside
1.0
0.9
0.5
0.1
ψ²
ψ²
ψ²
r
r
r
(ii) Wave probability density
(iv) Significance of density contours
(vi) Significance of density sum

Fig. 21.8. Representations in two dimensions of the probability distribution for a hydrogen 1*s* wave function.

The wave function ψ must obey certain mathematical conditions, the important ones are:

1. ψ must always be finite at any point.

If ψ were to become finite at any point in space this would correspond to a certainity of finding the particle there, which would conflict with the uncertainity principle. This is shown Fig. 21.9.

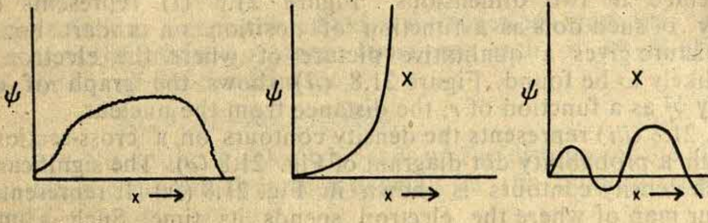


Fig. 21.9. Finite nature of ψ.

2. ψ must be single-valued at any point in space.

There can clearly be only one value of the probability of finding the particle at a given point in space. This is shown in Fig. 21.10.

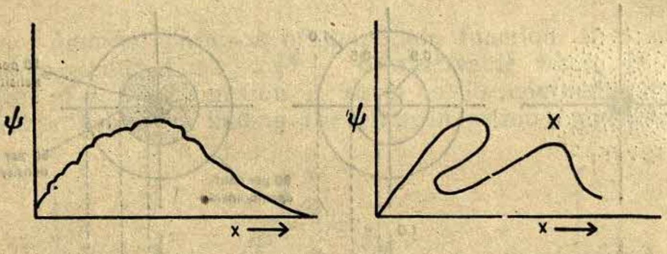


Fig. 21.10. ψ must be single valued.

3. ψ must be continuous.

If the probability of finding a particle at point x has a given value, that at $(x+\delta x)$ must be similar as $\delta x \rightarrow 0$. If this were not so,

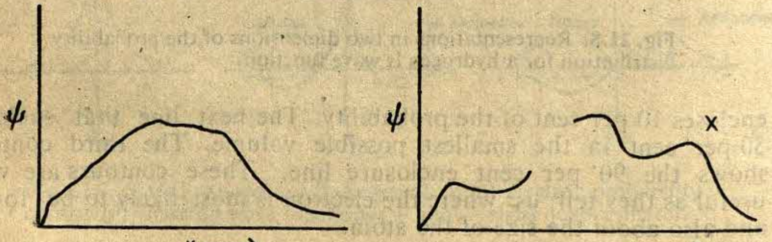


Fig. 21.11. Continuity of ψ.

the double differentiation in the Schrödinger equation could not be performed. An important consequence of this condition is that ψ must become zero at infinity. This is shown in Fig. 21.11.

21.9. APPLICATION OF SCHRODINGER EQUATION PARTICLE IN ONE DIMENSIONAL BOX

The most elementary application of Schrödinger equation is to study the effect of imposing a constraint upon the free particle by requiring that its motion be confined within fixed boundaries. In three dimensions, this is the problem of a particle enclosed in a box. The problem is further simplified if the box is a one dimensional box. In this case, a particle is required to move between set points on a straight line. The potential function that corresponds to such a condition is shown in Fig. 21.12.

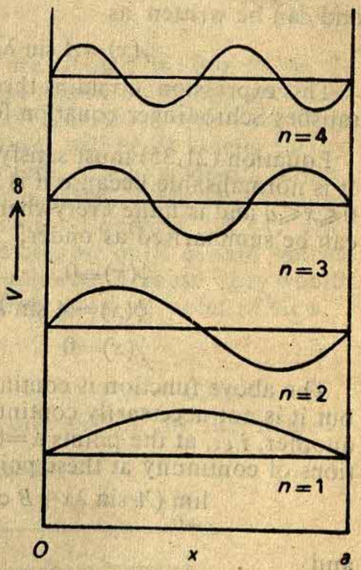


Fig. 21.12. Electron in a one dimensional box. Allowed electron waves and energy levels.

One dimensional Schrödinger equation can be written as,

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2}+V(x)\,\psi=E_n\psi \qquad \ldots(21.27)$$

One dimensional box is defined by a potential that is zero for $0 \leqslant x \leqslant a$ and infinite elsewhere. Algebraically, the potential is given by

$$\begin{aligned} V(x)&=\infty & x&<0 \\ V(x)&=0 & 0&\leqslant x\leqslant a \\ V(x)&=\infty & a&<x \end{aligned} \qquad \ldots(21.28)$$

Since the particle cannot move outside the box, we have the following condition *i.e.*,

$$\psi(x)=0 \qquad x \lessdot 0 \text{ and } x \gtrdot a \qquad \ldots(21.29)$$

The Schrödinger equation inside the box can be written as:

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2}=E_n\phi \qquad \ldots(21.30)$$

where E_n must be real and positive quantity. Let us introduce a new parameter λ which is defined as:

$$\frac{\pi^2 m E_n}{h^2}=\lambda^2 \qquad \ldots(21.31)$$

Now the Schrödinger equation can be written as

$$\frac{d^2\psi}{dx^2}=-\lambda^2\psi \qquad \ldots (21.32)$$

This is a differential equation and has two solutions, *i.e.*,

$$\psi_1(x)=\sin \lambda x \qquad \ldots (21.33)$$

and

$$\psi_2(x)=\cos \lambda x \qquad \ldots (21.34)$$

The general solution is a linear combination of the two solutions and can be written as

$$\psi(x)=A \sin \lambda x+B \cos \lambda x \qquad \ldots (21.35)$$

This expression contains three parameters, *i.e.*, A, B and λ and satisfies Schrödinger equation for any values of these parameters.

Equation (21.35) must satisfy the criterion of a wave function. It is normalisable because it is non-zero only in the finite interval $0 \leqslant x \leqslant a$ and is finite everywhere within the interval. These results can be summarised as under,

$$\begin{array}{ll} \psi(x)=0 & x<0 \qquad \ldots (21.36) \\ \psi(x)=A \sin \lambda x+B \cos \lambda x & 0\leqslant x\leqslant a \\ \psi(x)=0 & a<x \end{array}$$

The above function is continuous within any of the three intervals, but it is not necessarily continuous if we go from one interval to another, *i.e.*, at the points $x=0$ and $x=a$. On imposing the conditions of continuity at these points, we get

$$\lim_{x\to 0} (A \sin \lambda x+B \cos \lambda x)=B=0 \qquad \ldots (21.37)$$

and

$$\lim_{x\to a} (A \sin \lambda x+B \cos \lambda x)$$

$$=A \sin \lambda a+B \cos \lambda a=0 \qquad \ldots (21.38)$$

Since $B=0$, equation (21.38) can be written as:

$$A \sin \lambda a=0 \qquad \ldots (21.39)$$

In the above equation the parameter A cannot be zero, as this would mean the value of wave function to be zero everywhere. This will lead to zero probability of finding the particle which does not make any sense, we have the condition

$$\sin \lambda\, a=0 \qquad \ldots (21.40)$$

This equation has infinite number of solutions *i.e.*,

$$\lambda a=n\pi,\ n=0,\ \pm 1,\ \pm 2,\ \pm 3\ldots \qquad \ldots (21.41)$$

$n=0$, would mean the wave function to be zero everywhere, hence this is not allowed. Since $n=\nu$ and $n=-\nu$ lead to the same probability density function. Hence the possible values of n are

$$n=1, 2, 3, 4$$

Squaring both sides of (21.41)

$$\lambda^2a^2=n^2\pi^2 \qquad \ldots (21.42)$$

From equation (21.31)

$$\lambda^2=\frac{8\pi^2m\,E_n}{h^2} \qquad \ldots (21.43)$$

On comparing equations (21.42) and (21.43) we get

$$E_n=\frac{n^2h^2}{8ma^2} \qquad \ldots (21.44)$$

The first four of these energy levels are shown in Fig. 21.12. It follows from the above equation that the kinetic energy E_n decreases as the value of a increases. This means that more the room the electron has in which to move, the lower will be its kinetic energy which means greater stability of the system. Such a delocalisation of the motion of the electron can occur in certain kinds of structures like conjugated and aromatic compounds. Equation (21.44) also leads to the concept of stationary states because only certain values are allowed. All other values are not allowed because they would lead to results that do not make sense from physical point of view.

21.9. HYDROGEN ATOM

Consider a hydrogen atom containing one proton in the nucleus

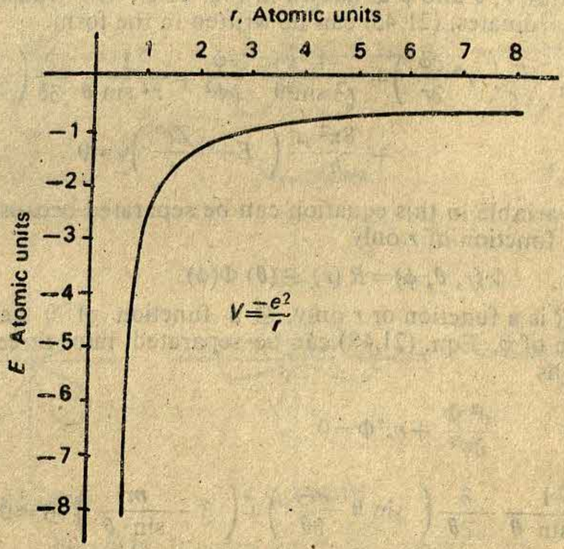


Fig. 21.13. Coulombic potential energy of negative electron in the field of positive proton.

and an electron moving around it. If we neglect the translational motion of the atom as a whole and the motion of the atomic nucleus, the problem of the hydrogen atom can be reduced to that of a single electron of mass m in a coulombic field. The motion of the nucleus can be taken into account by using reduced mass μ instead of m. The problem is similar to that of a particle in a three dimensional box. In this case there is spherical symmetry and instead of steep walls and zero potential energy within, there is a gradual rise in potential with distance from the nucleus $r=\infty$, $V=0$; at $r=0$, $V=-\infty$. The potential energy of the electron in the field of the nucleus of charge Ze is given by $V=-\frac{Ze^2}{r}$. This is plotted in Fig. 21.13.

The Schrödinger equation can be written as:

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi+\frac{8\pi^2\mu}{h^2}\left(E+\frac{Ze^2}{r}\right)\psi=0 \quad \ldots (21.45)$$

or $$\nabla^2\psi+\frac{8\pi^2\mu}{h^2}\left(E+\frac{Ze^2}{r}\right)\psi=0 \quad \ldots (21.46)$$

where $\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$.

The spherical symmetry of the potential energy function suggests that the equation may be solved most readily in spherical polar coordinates, r, θ and ϕ as shown in Fig. 21.6. On transforming into polar coordinates, (21.45) can be written in the form,

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\phi}{\partial r}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)$$
$$+\frac{8\pi^2\mu}{h^2}\left(E+\frac{Ze^2}{r}\right)\psi=0 \quad \ldots (21.47)$$

The variable in this equation can be separated because the potential is a function of r only

$$\psi(r,\theta,\phi)=R(r)\,\Theta(\theta)\,\Phi(\phi) \quad \ldots (21.48)$$

where R is a function or r only, Θ a function of θ only and Φ a function of φ. Eqn. (21.48) can be separated into three differential equations

$$\frac{\partial^2\Phi}{\partial\varphi^2}+m^2\Phi=0 \quad \ldots (21.49)$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\left(\beta-\frac{m^2}{\sin^2\theta}\right)\Theta=0 \quad \ldots (21.50)$$

and $$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{\beta}{r^2}R+\frac{8\pi^2\mu}{h^2}\left(E+\frac{Ze^2}{r}\right)R=0 \quad \ldots (21.51)$$

where m and β are constants. The boundary conditions for solutions of (21.49) are such that satisfactory values of Φ can be obtained only for $m=0, \pm 1, +2$ etc. On substituting these values of m into (21.50) and the equation solved for Θ, then permissible values of the latter are obtained only for $\beta=l(l+1)$, where $l=|m|, |m|+1, |m|+2$ etc. $|m|$ being the absolute values of m. With these values of β (21.51) yields satisfactory solutions only for values for a total quantum number $n=0, 1, 2, 3$ etc. Solution of (21.47) yields the total energy E of the electron in the atom, given by the expression;

$$E=-\frac{2\pi^2\mu Z^2e^4}{n^2h^2} \qquad \ldots (21.52)$$

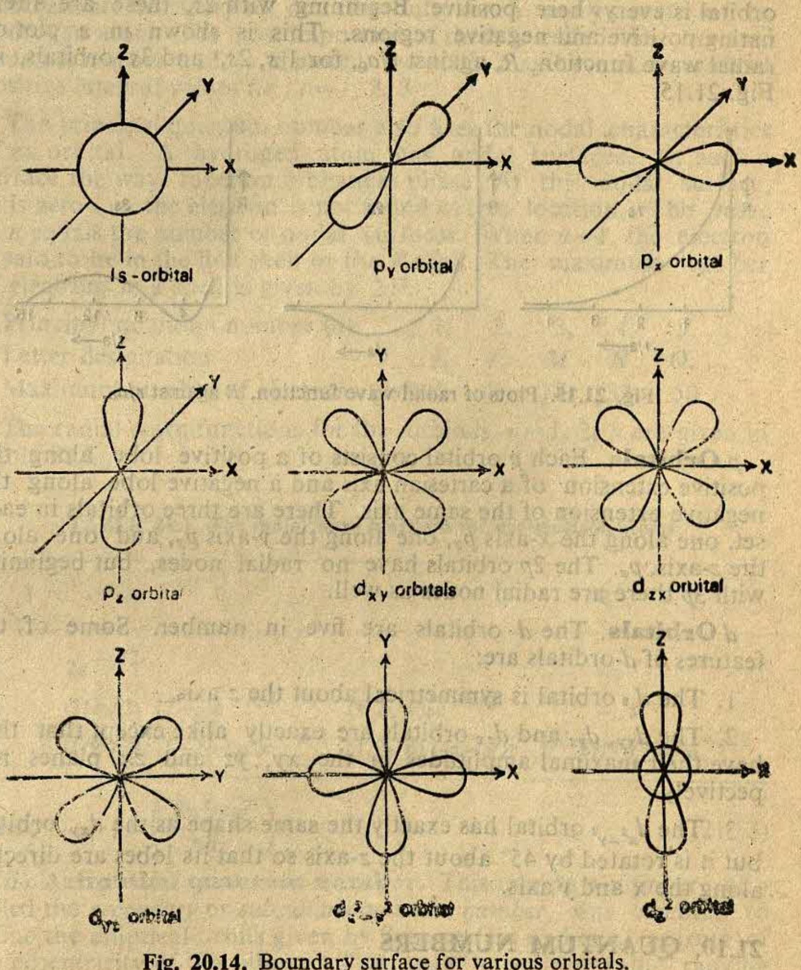


Fig. 20.14. Boundary surface for various orbitals.

where μ is the reduced mass of the nucleus and electron. This expression becomes identical with that from the old quantum theory of Bohr.

The boundary conditions require certain constants that enter into the solution of Schrödinger equation. These constants are called **quantum numbers**. The wave functions ψ which are solutions of the wave equation are commonly called **orbitals**. Orbitals for which $l=0, 1, 2$ and 3 are called the *s*, *p*, *d* and *f* orbitals respectively. Orbitals which are used, are shown in the form of three dimensional angular dependence diagrams. Fig. 21.14 gives the boundary surface diagrams for *s*, *p* and *d* orbitals.

***s* Orbitals**. Every *s* orbital is spherically symmetrical. The 1 *s* orbital is everywhere positive. Beginning with 2*s*, these are alternating positive and negative regions. This is shown in a plot of radial wave function, *R*, against r/a_0, for 1 *s*, 2*s*, and 3*s* orbitals, in Fig. 21.15.

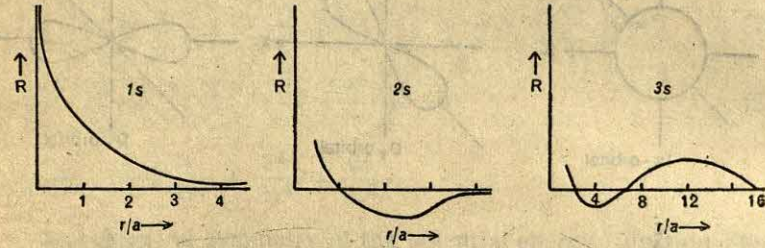


Fig. 21.15. Plots of radial wave function, *R* against r/a_0.

***p* Orbitals**. Each *p* orbital consists of a positive lobe along the positive extension of a cartesian axis and a negative lobe along the negative extension of the same axis. There are three orbitals in each set, one along the *x*-axis p_x, one along the *y*-axis p_y, and one along the *z*-axis, p_z. The 2*p* orbitals have no radial nodes, but beginning with 3*p* there are radial nodes as well.

***d* Orbitals**. The *d* orbitals are five in number. Some of the features of *d*-orditals are:

1. The d_{z^2} orbital is symmetrical about the *z* axis.

2. The d_{xy}, d_{yz} and d_{zx} orbitals are exactly alike except that they have their maximal amplitudes in the *xy*, *yz* and *zx* planes respectively.

3. The $d_{x^2-y^2}$ orbital has exactly the same shape as the d_{xy} orbital, but it is rotated by 45° about the *z*-axis so that its lobes are directed along the *x* and *y* axis.

21.10. QUANTUM NUMBERS

In order to define an electron in an atom completely and to explain the complex spectra of elements, we need four quantities known as quantum numbers. In a simple way this corresponds to a normal post office address. To characterise a particular Mr X it is necessary to allot a particular address to him, *i.e.*, Mr X, 256, Parliament Street, New Delhi, India. The country corresponds to the principal quantum number, the town to the subsidiary quantum number, the street to the spin quantum number and the street number to the magnetic quantum number.

(*i*) **Principal quantum number.** The Schrödinger wave equation for the hydrogen atom describes the electron wave in three dimensions. It is entirely appropriate then, that three integral numbers are necessary to describe fully each energy state of the hydrogen atom. The most important of these is called the *principal quantum number* and is denoted by n. It may have non-zero and positive integral values *i.e.*, $n=1, 2, 3 \ldots$

The principal quantum number also fixes the nodal characteristics of an orbital. A hydrogen atom has nodal surfaces. At such a surface the wave function ψ changes phase. At this nodal surface, ψ^2 is zero *i.e.*, the electron is not found at this location. The value of n equals the number of nodal surfaces. When $n=1$ the electron is said to be in the first shell or the K shell. The maximum number of electrons in a shell is given by $2n^2$.

Principal quantum number (n)	1,	2,	3,	4,	5. . .
Letter designation	K	L	M	N	O. . .
Maximum number of electrons ($2n^2$)	2	8	18	32	50

The radial wave functions for the orbitals $n=1, 2, 3$ are given in Table 21.1.

TABLE 21.1. The radial wave functions for one-electron atoms

n \ 1	0	1	2
1	$2e^{-\rho/2}$	–	–
2	$(1/2\sqrt{2})\ (2-\rho)e^{-\rho/2}$	$(1/2\sqrt{6})\rho e^{-\rho/2}$	–
3	$(1/9\sqrt{3})\ (6-6\rho+\rho^2)e^{-\rho/2}$	$(1/9\sqrt{6})\ (4\rho-\rho^2)e^{-\rho/2}$	$(1/9\sqrt{30})\rho^2 e^{-\rho/2}$

where
$$\rho=\left(\frac{8\pi^2 me^2}{nh^2}\right)r. \qquad \ldots (21.53)$$

(*ii*) **Azimuthal quantum number.** This quantum number, also called the *secondary* or *subsidiary quantum number*, was essential to define the elliptical orbits given by Sommerfeld and is a measure of the eccentricity of the ellipse. This may have any value ranging from $l=0$ to $n-1$.

It also relates to the nodal pattern of the orbital. There are l

nodal surfaces with angular dependence. Since there is a total of n nodal surfaces, there must be $(n-l)$ nodal surfaces without angular dependence *i.e.*, spherically symmetric. For the value of $n=2$, l can be either 0 or 1. If $l=0$ there are no nodal surfaces with angular dependence; the two radial nodal surfaces are both spherical in shape. One of these is the surface at r=infinity. For $l=1$, there is one angular dependent nodal surface, a plane. The second nodal surface $(n-l=2-1=1)$ is a sphere, again the nodal surface at infinity. Figure 21.16 shows cross-sectional views of the probability distributions corresponding to $n=1$ and $n=2$. The change of phase at the nodal surface is designated by plus and minus signs. If $n=1$, $l=0$ it represents $1s$ orbital for $n=2$, $l=0$ and 1 correspond to $2s$ and $2p$ orbitals.

The orbital angular momentum of an electron can be given by

$$\sqrt{\frac{l(l+1)\,h}{2\pi}} \qquad \ldots (21.54)$$

where h is Planck's constant.

(*iii*) **Magnetic quantum number**. As we have seen in case of Zeeman Effect. there are additional lines which appear in the magnetic field. To explain this splitting of spectral lines, a new quantum number was introduced, known as magnetic quantum number, m. This can have as many as $(2l+1)$ different values for a given value of l, starting from $-l$, 0, $+l$ and each value corresponds to one orbital.

The s subshell has only one orbital as $l=0$, $m=0$, a p subshell has 3 orbitals, $l=1$, $m=(2+1)=3$ and d has 5 orbitals and f seven. In these orbitals the difference of energies is very slight from one another.

(*iv*) **Spin quantum number**. This quantum number describes the spin of the electron about its own axis. Since spin can be either clockwise or anti-clockwise, spin quantum number has only two values $+\frac{1}{2}$ and $-\frac{1}{2}$. They are put as ↑ and ↓.

21.11. PAULI'S EXCLUSION PRINCIPLE

The three quantum numbers, n, l and m are needed to define an orbital. Each orbital may hold up to two electrons, so an extra-quantum number is required to define the spin of an electron in an orbital. The exclusion principle originates from studies by W. Pauli connected with the electron spin. Consider a system containing two electrons *i.e.*, helium atom. If each electron possesses one of the two spins, four different arrangements are possible for the two electrons as shown

⇅ ⇅ ⇅ ⇅

where the up or down arrows represent $+\frac{1}{2}$ or $-\frac{1}{2}$ values of the spin quantum number. Spectral observations by Pauli led him to conclude that some states do not exist and that therefore some spin combinations must be excluded. The Pauli principle can be stated in many ways. A simple form is that no two electrons can have the same values for the four quantum numbers. Each electron in an atom is unique and can be described in a way which distinguishes it from all the others. Indeed this must be so, for if two electrons in an atom could be described by the same set of quantum numbers, this would be saying that they both occupy the same position at the same time and are identical in every way and so would be indistinguishable from a new particle of double the mass and charge.

For example according to $2n^2$ rule, $n=2$ must have 8 electrons. According to Pauli's exclusion principle we can arrange them, having the following combinations:

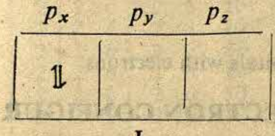
$n=2$	$l=0$	$m=0$	$s=+\frac{1}{2}$
$n=2$	$l=0$	$m=0$	$s=-\frac{1}{2}$
$n=2$	$l=1$	$m=0$	$s=+\frac{1}{2}$
$n=2$	$l=1$	$m=0$	$s=-\frac{1}{2}$
$n=2$	$l=1$	$m=+1$	$s=+\frac{1}{2}$
$n=2$	$l=1$	$m=+1$	$s=-\frac{1}{2}$
$n=2$	$l=1$	$m=-1$	$s=+\frac{1}{2}$
$n=2$	$l=1$	$m=-1$	$s=-\frac{1}{2}$

Similarly we can account for other levels.

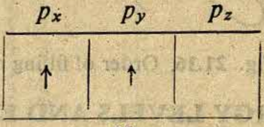
21.12. HUND'S RULE OF MAXIMUM MULTIPLICITY

This rule states that in an atom, the electrons in a sub-shell tend to remain unpaired as long as possible.

If we represent three p orbitals as boxes and electrons by arrows (↑ for $+\frac{1}{2}s$ and ↓ for $-\frac{1}{2}s$) then if two electrons are added to p-sub-shell, there exist two possibilities: I and II

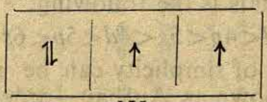


I



II

In the first arrangement, two electrons are in the same orbital (*i.e.* p_x) but it is not permitted by Hund's rule, so the II arrangement is right as this satisfies the rule. If we add third electron to this subshell, this will go to p_z (the third empty orbital) rather than to p_x and p_y. Pairing will be there if the fourth electron is added as shown in III.



III

Screening rule. According to this rule, the electrons filling the inner shells have the screening effect on the outer electrons against attraction by the nucleus.

This rule is responsible for the reason that every *ns* orbital is filled earlier than the corresponding $(n-1)$ *d* orbital. Also 5*s*, 5*p* and 6*s* orbitals are filled before 4*f* orbital.

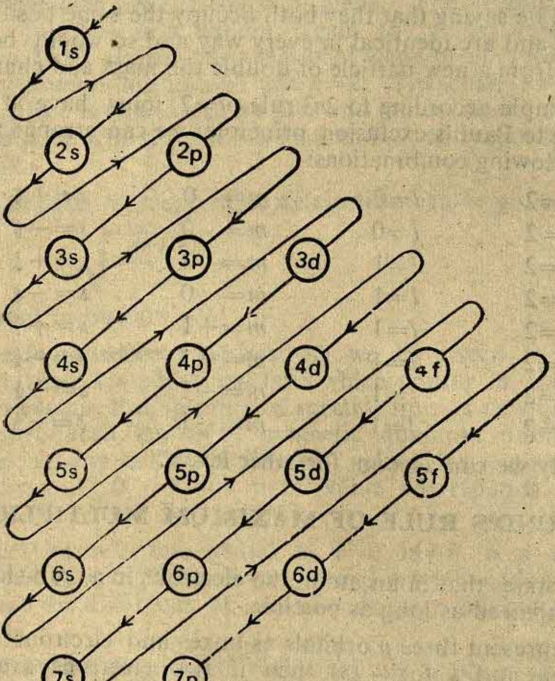


Fig. 21.16. Order of filling orbitals with electrons.

21.13. ENERGY LEVELS AND ELECTRON CONFIGURATION OF ELEMENTS

Distribution of electrons in orbitals for complicated atoms is governed by certain rules. As discussed earlier, each electron shell can have a maximum noumber of electrons given by $2n^2$. As each electron shell has subshells and their energy difference is very much less, the orbitals having lower energy are filled first. It is seen that the order of energy of various orbitals is the following;

$$1s<2s<2p<3s<3p<4s<3d<4p<5s<4d<5p<6s<4f<5d$$

The above order, for the sake of simplicity can be represented by a simple diagram (Fig. 21.16) known as Aufbau—order of orbitals, for feeding in electrons.

TABLE 21.2.
Arrangement of electrons in atoms

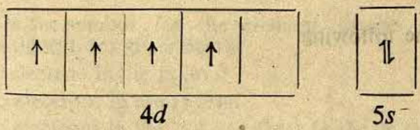
At. No.	Element	K	L		M			N				O				P	Q
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s6p6d6f	7s
1	H	1															
2	He	2															
3	Li	2	1														
4	Be	2	2														
5	B	2	2	1													
6	C	2	2	2													
7	N	2	2	3													
8	O	2	2	4													
9	F	2	2	5													
10	Ne	2	2	6													
11	Na	2	2	6	1												
12	Mg	2	2	6	2												
13	Al	2	2	6	2	1											
14	Si	2	2	6	2	2											
15	P	2	2	6	2	3											
16	S	2	2	6	2	4											
17	Cl	2	2	6	2	5											
18	Ar	2	2	6	2	6											
19	K	2	2	6	2	6		1									
20	Ca	2	2	6	2	6		2									
21	Sc	2	2	6	2	6	1	2									
22	Ti	2	2	6	2	6	2	2									
23	V	2	2	6	2	6	3	2									
24	Cr	2	2	6	2	6	5	1									
25	Mn	2	2	6	2	6	5	2									
26	Fe	2	2	6	2	6	6	2									
27	Co	2	2	6	2	6	7	2									
28	Ni	2	2	6	2	6	8	2									
29	Cu	2	2	6	2	6	10	1									
30	Zn	2	2	6	2	6	10	2									
31	Ga	2	2	6	2	6	10	2	1								
32	Ge	2	2	6	2	6	10	2	2								
33	As	2	2	6	2	6	10	2	3								
34	Se	2	2	6	2	6	10	2	4								
35	Br	2	2	6	2	6	10	2	5								
36	Kr	2	2	6	2	6	10	2	6								
37	Rb	2	2	6	2	6	10	2	6			1					
38	Sr	2	2	6	2	6	10	2	6			2					
39	Y	2	2	6	2	6	10	2	6	1		2					
40	Zr	2	2	6	2	6	10	2	6	2		2					
41	Nb	2	2	6	2	6	10	2	6	4		1					
42	Mo	2	2	6	2	6	10	2	6	5		1					
43	Tc	2	2	6	2	6	10	2	6	6		1					
44	Ru	2	2	6	2	6	10	2	6	7		1					
45	Rh	2	2	6	2	6	10	2	6	8		1					
46	Pd	2	2	6	2	6	10	2	6	10							
47	Ag	2	2	6	2	6	10	2	6	10		1					
48	Cd	2	2	6	2	6	10	2	6	10		2					
49	In	2	2	6	2	6	10	2	6	10		2	1				
50	Sn	2	2	6	2	6	10	2	6	10		2	2				

Arrangement of electrons in atoms

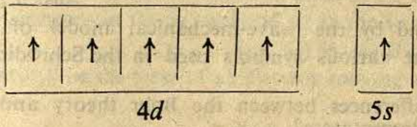
At. No.	Element	K	L		M			N				O				P				Q
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	6f	7s
51	Sb	2	2	6	2	6	10	2	6	10		2	3							
52	Te	2	2	6	2	6	10	2	6	10		2	4							
53	I	2	2	6	2	6	10	2	6	10		2	5							
54	Xe	2	2	6	2	6	10	2	6	10		2	6							
55	Cs	2	2	6	2	6	10	2	6	10		2	6			1				
56	Ba	2	2	6	2	6	10	2	6	10		2	6			2				
57	La	2	2	6	2	6	10	2	6	10		2	6	1		2				
58	Ce	2	2	6	2	6	10	2	6	10	2	2	6			2				
59	Pr	2	2	6	2	6	10	2	6	10	3	2	6			2				
60	Nd	2	2	6	2	6	10	2	6	10	4	2	6			2				
61	Pm	2	2	6	2	6	10	2	6	10	5	2	6			2				
62	Sm	2	2	6	2	6	10	2	6	10	6	2	6			2				
63	Eu	2	2	6	2	6	10	2	6	10	7	2	6			2				
64	Gd	2	2	6	2	6	10	2	6	10	7	2	6	1		2				
65	Tb	2	2	6	2	6	10	2	6	10	9	2	6			2				
66	Dy	2	2	6	2	6	10	2	6	10	10	2	6			2				
67	Ho	2	2	6	2	6	10	2	6	10	11	2	6			2				
68	Er	2	2	6	2	6	10	2	6	10	12	2	6			2				
69	Tm	2	2	6	2	6	10	2	6	10		2	6			2				
70	Yb	2	2	6	2	6	10	2	6	10	14	2	6			2				
71	Lu	2	2	6	2	6	10	2	6	10	14	2	6	1		2				
72	Hf	2	2	6	2	6	10	2	6	10	14	2	6	2		2				
73	Ta	2	2	6	2	6	10	2	6	10	14	2	6	3		2				
74	W	2	2	6	2	6	10	2	6	10	14	2	6	4		2				
75	Re	2	2	6	2	6	10	2	6	10	14	2	6	5		2				
76	Os	2	2	6	2	6	10	2	6	10	14	2	6	6		2				
77	Ir	2	2	6	2	6	10	2	6	10	14	2	6	7		2				
78	Pt	2	2	6	2	6	10	2	6	10	14	2	6	9		1				
79	Au	2	2	6	2	6	10	2	6	10	14	2	6	10		1				
80	Hg	2	2	6	2	6	10	2	6	10	14	2	6	10		2				
81	Tl	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1			
82	Pb	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2			
83	Bi	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3			
84	Po	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4			
85	At	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5			
86	Rn	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6			
87	Fr	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6			1
88	Ra	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1		2
89	Ac	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2		2
90	Th	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2		2
91	Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1		2
92	U	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1		2
93	Np	2	2	6	2	6	10	2	6	10	14	2	6	10	5	2	6			2
94	Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6			2
95	Am	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6			2
96	Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1		2
97	Bk	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1		2
98	Cf	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6			2
99	Es	2	2	6	2	6	10	2	5	10	14	2	6	10	11	2	6			2
100	Fm	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6			2
101	Md	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6			2
102	No	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6			2
103	Lw	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1		2
104	Ku	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	2		2
105	Ha	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	3		2

The electronic configuration of elements can be given by following the above rule along with Pauli's exclusion principle and Hund's Rule. Table 21.1 gives the electronic configuration of elements.

From the study of the said table, we find some departure from the Aufbau rule. The arrangement differs when the *d* level orbitals are either almost full as in the case of Cu, Pd, Ag, Pt and Au or half full as in Cr and Mo. Most of the cases can be explained in the light of one fact that completely filled, completely half filled and completely unfilled arrangements are more stable than any other. Thus d^5 and d^{10} configurations are much more stable than d^4, d^8 and d^9. Consider the configuration $4d^4$, $5s^2$ as shown below:



If one electron moves from 5*s* orbital to 4*d* orbital it becomes



In this case, 4*d* orbitals are completely half-filled. So this arrangement is preferred over the others. On the basis of the electronic configuration we can divide the elements in the periodic table into four general sections as shown in Fig. 21.17.

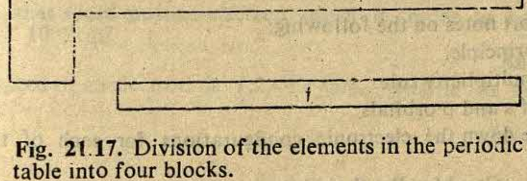


Fig. 21.17. Division of the elements in the periodic table into four blocks.

(1) *s*—block elements,
(2) *p*—block elements,
(3) *d*—block elements,
(4) *f*—block elements.

PROBLEMS

1. In the photo-electric effect, an absorbed quantum of light results in the ejection of an electron from the absorber. The kinetic energy of the ejected electron is equal to the energy of the light quantum absorbed minus the energy of the longest wave length quantum that causes the effect. Calculate the kinetic energy of a photo-electric electron produced in cesium by 4000Å light. The critical (maximum) wave length for the photo-electric effect in cesium is 6600Å.

Ans. K.E.$=1.96\times10^{-12}$ erg.

2. (*a*) Explain the uncertainty principle. How does it limit the description of the location of electrons in an atom?

(*b*) A snail of 1 g mass is travelling at a velocity of 0.1 cm/sec. What is the uncertainty in its position?

3. Write short notes on the following:

(*a*) Compton-effect.

(*b*) de-Broglie Relation.

(*c*) Zeeman Effect.

4. What is the wave length of a car with a mass of 1.3×10^{6} g moving at a speed of 1.0×10^{3} cm/sec?

Ans. 5.1×10^{-35} cm

5. What do you understand by the wave-mechanical model of the atom? Explain the meaning of the various symbols used in the Schrödinger's equation.

6. What are the major differences between the Bohr theory and the wave mechanical theory of the hydrogen atom?

7. What is Pauli's exclusion principle? How does it affect the arrangement of electrons in an atom?

8. Explain what is meant by:

(*a*) a shell;

(*b*) a subshell; and

(*c*) an electron orbital.

9. (*a*) Explain the term 'quantum numbers'. Give a brief account of the four quantum numbers.

(*b*) Show that the maximum number of electrons in the *M* shell ($n=3$) is 18.

10. Write short notes on the following:

(*a*) Aufbau principle.

(*b*) Hund's multiplicity rule.

(*c*) Shapes of s and p orbitals.

11. (*a*) Write down the electronic configurations for each of the following elements:

Ca; Mn; Br; S; and Ar.

(*b*) To what neutral atoms correspond the following electronic arrangements?

(*i*) $1s^2, 2s^2, 2p^6,$

(*ii*) $1s^2, 2s^2, 2p^6, 3s^2\ 3p^6\ 3d^5, 4s^1,$

(*iii*) $1s^2, 2s^2, 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^1,$

(*iv*) $1s^2, 2s^2\ 2p^6, 3s^2\ 3d^7, 4s^2;$

(*v*) $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^6\ 4d^{10}, 5s^2\ 5p^6, 5d^1, 6s^2.$

Ans. (*i*) Ne, (*ii*) Cr, (*iii*) Cu, (*iv*) Co (*v*) La

12. (*a*) What is the difference between the size and shape of a 2p and a 3p orbital?

(*b*) Is there any difference between the energy of an electron in orbitals represented by the quantum numbers.

$n=3$; $l=2$; $m=+2$ and $n=3$, $l=2$, $m=-1$?

(*c*) Give the number of identical d-orbitals in a given energy level and the values of their m quantum numbers.

13. Which of the following statements concerning the function of the two quantum numbers are correct?

(*i*) n determines the shape of an orbital
(*ii*) l determines the size of an orbital
(*iii*) n determines the size of an orbital
(*iv*) l determines the shape of an orbital
(*v*) n determines the number of electron density in an orbital.

Ans. (*iii*) and (*iv*) are correct

14 Write the symbol for the element whose atoms have the outermost electron configurations given below:

(*a*) One electron in the 1s level
(*b*) Two electrons in the 1s level
(*c*) Two electrons in the 2s level, three in the 2p level
(*d*) One electron in the 3s level
(*e*) Two electrons in the 3s level and three in the 3p level.
(*f*) Two electrons in the 3s level and six in the 3p level.

Ans. (*a*) H, (*b*) He, (*c*) N, (*d*) Na, (*e*) P, (*f*) A.

15. What will be the mass of an electron moving with a speed of 5.00×10^9 cm $\sec^{-1}$?

Ans. 9.24×10^{-28} g

16. (*a*) In what ways do the spatial contributions of the orbitals in each pair differ from each other?

(*i*) 1s and 2s (*ii*) 2s and $2p_x$ (*iii*) $2p_x$ and $2p_z$.

(*b*) List all the elements whose atoms have only one electron in (*i*) p subshell (*ii*) in s subshell.

Ans. (*i*) Only group III_A elements (*ii*) Only group I_A elements.

17. (*a*) What is kinetic energy of an electron that has a deBroglie wavelength of 10^{-8} cm?

(*b*) Through what potential difference must it have been accelerated?

Ans. (*a*) 2.41×10^{-17} J (*b*) 151 V.

18. With what speed must an electron travel in order to have a de Broglie wavelength of 10^{-8} cm?

Ans, 7.28×10^6 m/s

19. The speed of an electron is 1.2×10^6 m/s. What is its de Broglie wavelength?

Ans. 6.06×10^{-10} m.

Chapter 22

CHEMICAL BONDING

22.1. INTRODUCTION

One of the most fundamental questions in chemistry is the nature of forces which hold the atoms together in a molecule. Historically Frankland in 1852 first introduced the concept of chemical bonding. According to him, valency is the combining capacity of an element in a compound. Thus nitrogen has a valency 3, oxygen two and hydrogen one. With this defination it was possible to characterise some elements with a valence which aided in predicting the formulas of some of their compounds.

The number of loosely bound electrons in an atom gives the respective valence of the atom. These loosely bound electrons may be involved in the formation of chemical bonds. This concept has recently been abandoned and replaced by more specific and informative terms. The modern use of the word "valence" is not as a noun but as adjective meaning associated with chemical bonding. Thus we regard valence electrons as most loosely bound to the atom which may be involved in the formation of chemical bonds.

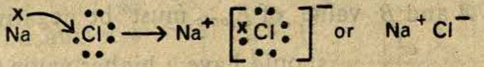
Another important feature of the theory of chemical bonding should be, to explain the geometry of the molecule and what is that makes one molecule linear and other bent ? From the energy considerations, chemical bonds are formed because in doing so atoms can follow the universal tendency of all mechanical systems to attain a state of lowest potential energy. Since in the formation of a bond a pair of atoms release certain amount of energy to their surroundings. This energy which is known as the bond dissociation energy must be imparted to the molecule in order to break a bond. As we proceed with the development of the subject we hope to find an explanation for the fact as to why the bond formation leads to the lowering of energy of the system. Chemical bonding may also be defined as the phenomenon involving the union of two or more atoms through redistribution of electrons in their outer shells, either by sharing of electrons among themselves or by transference of electrons from one atom to another. Since the inert gases contain eight electrons except for helium which contains two electrons. This configuration represents a state of maximum stability and hence minimum energy. Atoms of all other elements tend to acquire this stable configuration of inert gases. They do so either by the transfer of electrons from one atom to another or by mutual sharing of electrons. This mode of chemical bond formation was given by W. Kossel and G.N. Lewis in 1916. There are several ways in which atoms may obtain a stable electronic configuration by gaining losing or sharing electrons. The elements in the periodic table can be divided into (*i*) electropositive elements *i.e.*, the elements, whose atoms give up one or more electrons fairly readily (*ii*) electronegative elements which tend to take up electrons and (*iii*) elements which neither tend to gain or lose electrons. We can thus classify three types bonding as under:

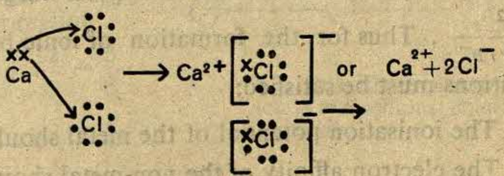
1. Electropositive element + Electronegative element	Ionic bond
2. Electronegative element + Electronegative element	Covalent bond
3. Electropositive element + Electropositive element	Metallic bond

22.2. IONIC OR ELECTROVALENT BOND

The ionic or electrovalent bond is formed when one or more electrons have been transferred from one atom to complete the orbitals of another atom. Elements which have a tendency to loose one or more electrons are called electropositive (*e.g.* alkali metals) while those having a tendency to gain electrons are called electronegative (*e.g.* halogens). Kossel pointed out the facts that when atoms of electropositive and electronegative elements combine together, one or more electrons are transferred from the former to latter and the atoms are converted into cations and anions. As a result of mutual electrostatic attraction between the ions so formed, an ionic or electrovalent bond is established.

Examples





The anions formed always achieve an inert gas configuration when forming ionic bond.

22.3. CONDITIONS FOR THE FORMATION OF IONIC BOND

The formation of an ionic molecule A^+B^- can be thought to occur through the following steps:

(*i*) Atom A gives up an electron by absorbing energy equal to its ionisation energy and is converted into cations A^+ ionisation

$$\text{energy} \xrightarrow{-e^-} A^+ + e^-$$

(*ii*) In the second step the atom B picks up the electron released by A and is converted into anion B^-. In this process the energy equal to electron affinity of B is released.

$$B + e^- \xrightarrow{e} B^- + EA \text{ (Energy released)}$$

(*iii*) In the third step, cation A and anion B combine together due to electrostatic attraction, to give a stable ionic crystal A^+B^-. In this process energy equal to the heat of formation of the ionic compound A^+B^-, is released

$$A^+ + B^- \longrightarrow A^+B^- + \text{energy released}$$

Heat of formation is equal to $-e/r_A{}^+ + r_B{}^-$, where negative sign indicates the release of energy. Here e is ionic charge on A^+ and B^- and $r_A{}^+$ and $r_B{}^-$ are ionic radii of A^+ and B^- respectively. Thus

$$\left(-\frac{e^2}{r_A{}^+ + r_B{}^-}\right) = \text{Energy released}$$

Thus the overall energy change, E_{ionic} in the formation of ionic crystal is given by

$$E_{ionic} = +(IP)_A - (EA)_{B}{}^- \frac{e^2}{r_A{}^+ + r_B{}^-}$$

Now if the bonded ions, A^+ and B^-, are more stable than the free atoms A and B value of E_{ionic} must be negative. To fulfil this condition $\frac{e^2}{r_A{}^+ + r_B{}^-}$ should have a higher value than $(IP)_A - EA_B$ when this condition is fulfilled we shall get a larger negative value of $\frac{e^2}{r_A{}^+ + r_B{}^-}$. Thus for the formation of ionic bonds the following conditions must be satisfied:

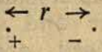
(*i*) The ionisation potential of the metal should be low.

(*ii*) The electron affinity of the non-metal should be high.

(*iii*) The lattice energy of the compound formed should be high.

22.4. CALCULATION OF LATTICE ENERGIES

Consider two point charges separated by a distance



The force f acting between them is given according to Coulomb's law

$$f=\frac{e^2}{r^2}$$

where e is the electronic charge. The potential energy, V, that is the energy required to separate them to infinite distance, is given by the equation

$$V=\frac{e^2}{r}$$

The negative sign arises because it is convenient to take potential energy to be zero when the ions are separated to infinity. If consider a linear array with a regular separation r; Fig. 22.1

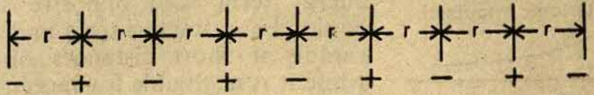


Fig. 22.1.

The energy of the given ion I, due to the presence of the others which exert Coulombic forces on it, is

$$V_1=-e^2\left(\frac{2}{r}-\frac{2}{2r}-\frac{2}{3r}-\frac{2}{4r}\cdots\cdots\right)$$

As can be seen from Fig. 22.2, a given ion A has six nearest neighbours, twelve next nearest and so on. Substituting the numbers at various distances we can write for the potential energy of an ion A due to coulombic forces, the expression,

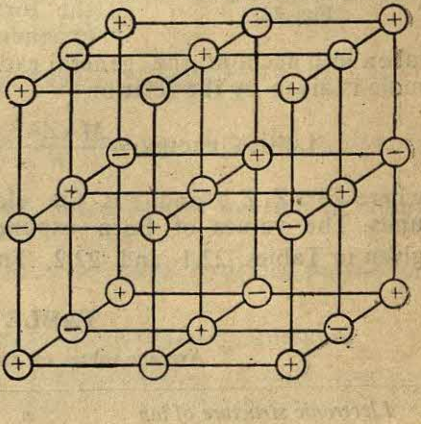


Fig. 22.2. Environment for ion A in a sodium chloride structure.

$$V_A=\frac{-e^2}{r}\left(\frac{6}{1}-\frac{12}{2}-\frac{8}{3}-\frac{6}{4}+\cdots\cdots\right)$$

$$=\frac{-Me^2}{r}$$

where r is the distance between centres of nearest neighbours. The quantity inside the bracket should be summed to infinite. It depends only on the geometry and not on the chemistry *i.e.*, it will have the same value for all face centred cubic crystals. There will be such a constant for each crystal structure and such constants are called Madelung constant. The generalised energy expression can be written as

$$\frac{-Me^2Z_+Z_-}{r}$$

where Z and Z are the number of charges on the positive and negative ions and $r=r_++r_-$. In addition to the coulombic forces we should also include the interionic repulsive forces which become appreciable when the two ions with opposite charges approach closely.

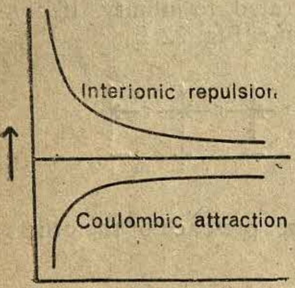


Fig. 22.3.

As the two ions approach closer, their electron shells begin to overlap the forces rise rapidly and the interionic repulsion also increases sharply, as shown in Fig. 22.3. The energy term is of opposite sign to the coulombic attractive term and rises very rapidly at short distances of approach while it is negligible for larger distances. The curve for coulombic terms varies as $\frac{1}{r}$. The curve for the repulsion terms can be described by a function of the form where n is known as Born exponent. When the repulsive term is taken into account, the general expression for the lattice energy per mole is given by the relation

$$\text{Lattice energy}=\frac{MNZ^2e^2}{r}\left(1-\frac{1}{n}\right)$$

where $Z^2=Z_+Z_-$, and e is the electronic charge in electrostatic units. The values of Born exponent and Mandelung constant are given in Tables 22.1 and 22.2. The lattice energies of the alkali

TABLE 22.1.

Average values for the Born exponent

Electronic structure of ion	*n*	*Example*
He	5	Li^+, Be^{2+}
Ne	7	Na^+, Mg^{2+}, O^{9-}, F^-
Ar	9	K^+, Ca^{2+}, S^{9-}, Cl^-, Cu^+
Kr	10	Rb^+, Br^-, Ag^+
Xe	12	Cs^+, I^-, Au^+

TABLE 22.2

Values of the Madelung constant for various structures

Sodium chloride	1.747558
Cesium chloride	1.762670
Zinc blende	1.63806
Wurtzite (ZnS)	1.641
Fluorite (CaF_2)	5.03878
Rutile (TiO_2)	4.816
Cadmium iodide	4.71
Quartz (SiO_2)	4.4394

TABLE 22.3

Lattice energies (Kcal) of alkali halides

Elements	*Fluoride*	*Chloride*	*Bromide*	*Iodide*
Lithium	2401	199.2	188.5	174.1
Sodium	213.4	183.1	174.5	163.9
Potassium	189.7	165.4	159.3	150.8
Rubidium	181.6	160.7	153.5	145.3
Cesium	173.7	152.2	146.3	139.1

halides have been calculated with the help of formulas of this type and have been found to be in close agreement with those values which have been determined experimentally. The calculated values of alkali halides are shown in Table 22.3.

22.5. APPLICATIONS OF LATTICE ENERGY

Lattice energy finds numerous applications some of them are as under:

(*i*) In the discussion of special properties of fluorine in relation to other halogens.

(*ii*) In the account of stabilities of metal hydrides polyhalides, peroxides, and superoxide.

(*iii*) In the derivation of crystal field stabilisation energies.

(*iv*) In the discussion of the characterisation of high oxidation states of metals as fluorides and their low oxidation states as iodides.

The Born-Haber Cycle

The direct determination of the lattice energy of an ionic crystal has been carried out for only a few compounds. In the majority of cases it is not possible to measure this energy directly; however a cyclic process has been devised by Born and Haber which relates the crystal energy to other thermochemical quantities where the energy of formation of a crystal from its component elements is known, it is possible to dissect this value into the energies of a number of processes, which may be postulated as constituting the intermediate steps in the formation of the crystal. By means of this circuitious procedure it is possible to calculate algebraically the theoretical lattice energy of a crystal. For example, formation of sodium chloride from elementary gaseous chlorine. It may be assumed that the sodium metal is evaporated and the diatomic chloride is dissociated; then the alkali atoms are ionized and the electrons so obtained are transferred to the halogen atom so that positive sodium ions and negative chloride ions are left in the gaseous phase. As indicated diagrammatically in Fig. 22.4 the energy of sublimation of metallic sodium is *S*, the ionisation energy of gaseous sodium is *I*, the energy of dissociation of Cl_2 is *D*, the electron affinity of the chlorine atom is *E* and the lattice energy of the solid NaCl is U_O. The heat of the formation of crystals from its elementary elements is designated as *Q*.

The total energy of formation of the crystal from its elementary compounds is given by the equation

$$-Q=S+D+IE-EA-U_O$$

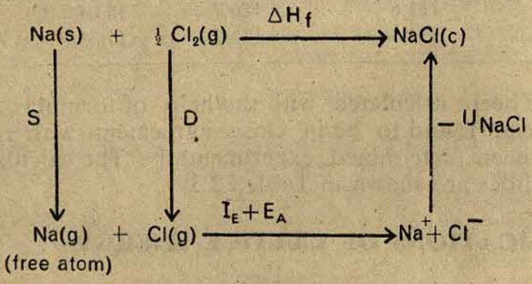


FIG. 22.4. Born Haber cycle.

The value of *Q* is accurately known experimentally for many substances and where the other thermochemical values are available, it is possible to solve for the lattice energy be rearranging the aforesaid equation as given below:

$$U_O=Q+S+D+I_E-E_A$$

Examples. Calculate the lattice energy of NaCl crystal from the following data by use of Born Haber cycle. Heat of Sublimation for Na is 26.0 kcal/g, dissociation energy of molecular chlorine $=57.2$ kcal(g), potential energy for sodium atom, *I* 117.9 kcal/g, electron affinity of chlorine atom, $-E$ -86.5 kcal/g, heat of formation of NaCl$=98.2$ kcal/g.

Lattice energy U_O?

$-98.2=26+(57.2)+117.9-85.5-U_O$

$U(\text{NaCl})=-98.2-28.6-117.9+86.5=184.2$ kcal/g

Uses of Born Haber Cycle

Born-Haber cycle can be used for the determination of electron affinities of elements which are difficult to determine by other methods.

Example. Calculate the electron affinity of iodine with the help of the following data:

$$(Q \text{ for})_{\text{NaI}} = -68.8 \text{ (kcal/g)}, (S)_{\text{Na}} = 25.9 \text{ kcal(g)};$$

$$U_0 = 25.5 \text{ kcal/g}$$

$$(I)_{\text{Na}} = 1184 \text{ kcal/g } U_{\text{NaI}} = -165.4 \text{ kcal/g}$$

$$E = -68.8 - 25.9 - 25.5 - 118.4 + 165.4$$

$$= -73.2 \text{ kcal/mole}$$

Born Haber cycle helps rationalise the existence of certain compounds and the non-existence of others. Born Haber cycle provides interesting insights into the energy factors operating in ionic compound.

22.6. IONIC RADII

The size of ions is determined by the attractive force exerted on the outerelectrons by the effective nuclear charge *i.e.* the true nuclear charge diminished by the effect of the inner or screening electrons. When a neutral atom is converted into a positive ion its size is expected to decrease since there has been a net increase in effective nuclear charge. On the other hand, there should be an increase in size when a negative ion is formed from the neutral atom. The distance between neighbouring positive and negative ions in a crystal is called ionic Radii. Some values of the interionic distances in some alkali metal halides is given in Table 22.3.

If we subtract the interionic distance in a sodium halide from the interionic distance in the corresponding potassium compound, we get an almost constant value for the difference, △, as shown in Table 22.4.

TABLE 22.4

Interionic Distances

Interionic	*Distance/pm*	*(KF-NaF, etc.)*
KF	266	33
NaF	233	
KCl	314	
NaCl	281	33
KBr	329	
NaBr	298	31
KI	353	30
NaI	323	

This constancy can be explained if each ion acts as sphere of constant radius; the measured interionic distance between two ions in an ionic structure is assumed to be equal to the sum of the radii of two spheres in contact *i.e.*

$$d=r_{+}+r_{-}$$

Thus if we know the interionic distance and the radius of one of the ion, that of the other ion can thus be computed. It is thus possible to have a table of ionic radii

$$r_{-}=d-r_{+}$$

The interionic distances in case of crystals can be measured by the X-ray diffraction method. A discussion of trends in Chemical properties in relation to the periodic classification can often be linked with trends in ionic radii. A knowledge of ionic radii may be a guide to the structure of an ionic crystal.

22.7. PROPERTIES OF IONIC SUBSTANCES

There are several properties which distinguish ionic compounds from covalent compounds. These may be related rather simply to the structure of ionic compounds namely, a lattice composed of positive and negative ions such that the attractive forces between oppositely charged ions are maximized and the repulsive forces between ions of the same charge minimized.

(1) Ionic compounds do not conduct electricity in solid state but conduct electricity quite well when molten. The conductivity in the molten state is attributed to the presence of ions, atoms charged either positively or negatively, which are free to move under the influence of electric field. In the solid the ions are bound lightly in the lattice and are not free to migrate and carry electrical current.

(2) Ionic compounds show high melting and boiling points. Ionic bonds usually are quite strong and they are non-directional. Since in ionic solids, the ions are held together tightly, a considerably amount of energy is needed to dislodge them from the crystal lattice. For example high melting point of sodium chloride is due to strong electrostatic attraction between sodium cations and the chloride anions, and the lattice structure which results in each sodium ion attracting six chloride ions which in turn attracts six sodium ions throughout the crystal. The strong electrostatic forces existing in ionic solids also explain the low volatility and high boiling point.

(3) The ionic compounds usually are very hard but brittle substances. The hardness of the ionic substances follows naturally from the argument given above, except in this case we are relating the multivalent attractions between the ions with mechanical separation rather than separation through thermal energy. The tendency towards brittleness results from the nature of ionic bonding. If one

can apply sufficient force to displace the ions slightly, the formerly the attractive forces become repulsive as anion-anion and cation-cation contracts occur.

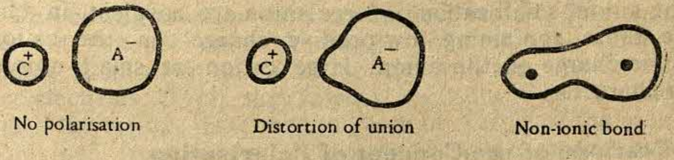
(4) Ionic compounds are often soluble in polar solvents with high dielectric constants. The energy of interaction of two charged particles is given by:

$$E = \frac{q^+q^-}{\varepsilon r}$$

where q^+ and q^- are charges, r, is the distance of separation and ε, is the dielectric constant which is 1.00 for free space and nearly the same for air. For common polar solvents, however, the dielectric constants have considerably higher values, the electrostatic forces of attraction between the ions weaken and get separated to one another to give solution.

22.8. COVALENT CHARACTER IN PREDOMINANTLY IONIC COMPOUND POLARISATION

When a cation approaches an anion closely, the net positive charge on the cation tends to attract the electron cloud of the anion towards itself due to the electrostatic force of attraction existing between them. At the same time the cation also tends to repel the positively charged nucleus of the anion. The combined effect of these two forces is that the electron cloud of the anion no longer remains symmetrical but it is elongated towards the cation as shown in Fig. 22.5. This is called distortion, deformation or polarisation of the anion by the cation and anion is said to be polarised. The ability of a cation to polarise a nearby anion is called its polarisation ability or polarisation power. The anion also has a similar effect on the cation *i.e.* the cation is also polarised by the anion. Since the size of a cation is generally smaller cation is polarised by the anion to a lesser extent *i.e.*, the polarisation of cation by an anion is considered almost negligible in most cases. The cations have a strong polarisation power and the anions are more susceptible to polarisation *i.e.*, the anions have more polarisability.



No polarisation Distortion of union Non-ionic bond

Fig. 22.5. Polarisation of an anion (A^-) by a cation (C^+).

Factors Affecting the Polarisation of an Ions—Fajans Rules

Fajans considered the effect which a small highly charged cation would have on an anion. Fajan suggested the following rules to estimates the extent to which a cation could polarize an anion and thus induce covalent character. Polarization will be increased by

(*i*) **Charge on the cation or anion**. Generally speaking the polarising power of a cation to polarise an anion increases with the increase in its positive charge. The reason is that a cation having higher charge can attract electrons more effectively. Thus in anhydrous chlorides viz., NaCl, $MgCl_2$ and $AlCl_3$ the polarising power of the cations Na^+, Mg^{2+} and Al^{3+} increase in order: Na^+, Mg^{2+}, Al^{3+}, since the positive charges on these cations also increase in the same order.

Similarly the polarisability of an anion also increases with the increase in its negative charge. This is because of the fact that with an increase in the negative charge, the anion will be able to repel its outermost electrons more effectively. Thus in fluorides and oxides of a metal cation O^{2-} ion is more polarised than F^- ion because F^- ion has only one negative charge while O^{2-} has two negative charges. This indicates that oxides are more covalent than fluorides.

(*ii*) **Size of the ion**. Polarising power of a cation depends upon its size. Polarising power of a cation increases as the size of cation decreases. For example, the polarising power of the IIA group cation having same charge decreases from Be^{2+} to Ba^{2+}, due to increase in their size.

(*iii*) **Electronic configuration of the cation.** A cation with 18 electrons in its outermost shell has greater polarising power to polarise an anion than a cation with 8 electrons in its outermost shell even if both the cations have the same size and charge. Fajans rules given above can be summarized by saying that the molecules containing high positive charge on the cation, high negative charge on the anion, small cation or large anion are covalent in character while those containing low positive charge on the cation, low negative charge on the anion, large cation or small anion show ionic character.

Applications of the Concept of Polarisation

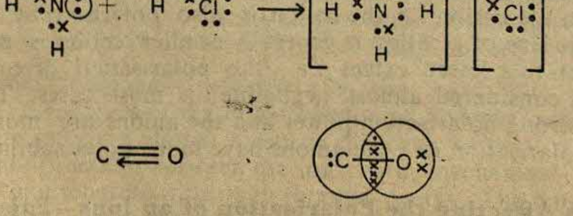


Fig. 22.6. Formation of Covalent bond.

It is also called charge density or ionic potential and can be represented as shown in Fig. 22.6.

General Characteristics of Covalent Compounds

(*i*) **Physical state**. Covalent compounds of low molecular weight are those which have high molecular weight (*i.e.* 10 dine). If they are solid at room temperature they are often soft. An increase in the polar character of the molecule increases the hardness.

(*ii*) **Crystal structure.** Solid covalent compounds possess crystalline lattices consisting of separate molecules. Within the crystal the individual molecules are held together by weak intermolecular forces.

(*iii*) **Melting point and boiling point**. Covalent compounds have low melting point and boiling point because the intermolecular forces are weak.

(*iv*) **Polar nature**. When two atoms which are not identical *i.e.* are not of equal electronegativity *e.g.* H and Cl, form a covalent bond.

(*v*) **Solubility**. Covalent compounds are commonly soluble in organic non-polar or weakly polar solvents but insoluble in water and polar solvents.

22.9. VARIABLE ELECTROVALENCY

There are a number of elements (transition or non-transiton) which show more than one valency in the formation of their compounds. This is due to the presence of unstable configuration of the core in them (transition metals) and inert pair effect in (heavier p-block elements).

(*i*) **The configuration of ions is not stable**. The valency of an element depends upon the number of electrons present in the outermost shell of an atom; these electrons are, therefore, termed valence electrons. If all the valency electrons from an atom are removed, the residue is termed the core or kernel of the atom. The core obtained from a normal element is stable, since it has 2 or 8 electrons. The configuration of cation, which show only one particular valency is shown below.

Na^+ $1s^22s^22p^6$, Mg^{2+} $1s^22s^2p^6$
K^+ $1s^22s^2p^63s^2ep^6$, Ca^{2+} $1s^22s^22p^63s^23p^6$

Several other ions particularly that obtained from a transition metal are unstable and one or more electrons may be removed from such configuration of the core to get ions with variable oxidation states.

Iron, cobalt and nickel form divalent as well as trivalent ions. The divalent ions resulting from the loss of two electrons from the utermost shell have 14, 15 and 16 electrons in their respective outermost shells as shown below:

Metal	Configuration of atoms	Ion	Configuration of ions
Fe	2, 8, $3s^2p^6d^64s^2$	Fe^{2+}	2, 8, $3s^2p^6d^6$
Co	2, 8, $3s^2p^6d^74s^2$	Co^{2+}	2, 8, $3s^2p^6d^7$
Ni	2, 8, $3s^2p^6d^84s^2$	Ni^{2+}	2, 8, $3s^2p^6d^8$

Evidently the outer configuration of the divalent ions are $s^2p^6d^x$ where x is 6, 7 or 8 respectively, in Fe^{2+}, Co^{2+} and Ni^{2+}. This configuration is not stable as the s^2p^6 configuration. Hence, these ions can easily loose one of the d-electrons producing there by the trivalent ions, namely Fe^{3+}, Co^{3+} and Ni^{3+}. These ions are, more stable since the effective positive charge on the nucleus is now higher and it prevents the elimination of any more electron.

(*ii*) **Inert pair effect**. Some heavier elements such as Sn and Pb show +2 and +4 oxidation states. Since Sn and Pb atoms belong to the VI group of periodic table, +4 state is called its group number oxidation state, G. These elements also exhibit +2 oxidation is +4 oxidation state is obtained by loosing all the valency electrons, while lower oxidation state +2 is obtained when only np electrons are lost and the ns electron pair, due to its extra stability, remains inert *i.e.* it is not lost. Such a pair of ns-electrons is called inert pair and the effect caused by it is known as inert pair effect. The reluctance of the s-electron pair to take part bond formation is known as inert pair effect.

For example

Gallium (At. No. 31) indium (40) and Thallium (81)

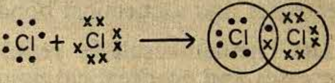
Atom or ion	*Electronic configuration*	*Remarks*
Ga	2, 8, 18, $3s^2p^1$	There are three valency electrons
Ga^+	2, 8, 18, $3s^2$	
Ga^{+3}	2, 8, 18	Only one 32 electron is lost
		All the three electrons are lost
In	2, 8, 18, 18, $4s^2p^1$	
In^+	2, 8, 18, 18, $4s^2$	
In^{+3}	2, 8, 18, 18	
T1	2, 8, 18, 32, 18, $5s^2p^1$	
$T1^+$	2, 8, 18, 32, 18, $5s^2$	
$T1^{+3}$	2, 8, 18, 32, 18	
Tin (At. No. 50)		
Sn	2, 8, 18, 18, $5s^2p^2$	There are four valency electrons
Sn^{2+}	2, 8, 18, 18 $5s^2$	
Sn^{4+}	2, 8, 18, 18	

The inert pair effect is also shown by antimony and bismuth the elements of Group V. All these elements show +3 and +4, +5 oxidation states.

Antimony

Sb	2, 8, 18, 18, $5s^2p^3$
Sb^{3+}	2, 8, 18, 18, $5s^2$
Sb^{+5}	2, 8, 18, 18
Bi	2, 8, 18, 32, 18, $6s^2p^3$
Bi^{+3}	2, 8, 18, 32, 18, $6s^2$
Bi^{+5}	2, 8, 18, 32, 18.

22.10. COVALENT BOND



Cl_2 molecule

G.N. Lewis in 1916 introduced the idea of the electron pair bond or covalent bond. He suggested that atoms of two elements may share electrons in the striving to attain the inert gas structure. According to Lewis theory an atom in forming a covalent bond must share not only an electron belonging to another atom but also one of its own electrons with the other atoms. Thus the covalent bond is one, produced by sharing of two electrons by two atoms. For example, the chlorine molecule is composed of two atoms of chlorine held together by a bond composed of two shared electrons. Each chlorine atom originaly had seven electrons in its outermost shell, but by mutual sharing of two electrons both atoms attain the electronic structure of inert gas argon.

Rules for Covalent Bond Formation

The following rules are useful for the formation of covalent bond.

(*i*) Normally two electrons pair up to form one bond.

(*ii*) The atomic orbitals on the bonding atoms must overlap.

(*iii*) For most molecules there will be a maximum of eight electrons in the valence shell.

(*iv*) For elements with available d-orbitals, the valence shell can be expanded beyond an octet.

(*v*) Electron-electron repulsion will be minimised.

(*vi*) It has been assumed implicitly in all of these rules that the molecule will seek the lowest energy.

Energies of Covalent Bond Formation

The formation of a chemical bond takes place only if the mutual approach of the atom is accompanied by a decrease in energy. When the two atoms are brought closer to one another, new forces of attraction and repulsion, are set in. The forces of attraction are between the nucleus of one atom for the electrons of the other. The forces of repulsion between the two nuclei amongst themselves as well as between the electron of two atoms amongst themselves. The forces of attraction and repulsion are presented in Fig. 22.7.

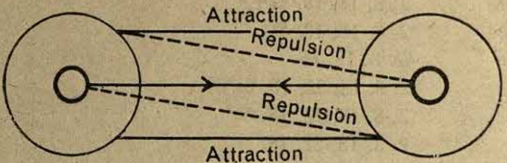


Fig. 22.7.

(*i*) If the net result is attraction, the total energy of the system decreases and a chemical bond results.

(*ii*) The net result is repulsion, the total energy of the system increases and no chemical bonding is possible.

Let us now consider the process of formation of hydrogen molecule from two hydrogen atoms. When the hydrogen atoms are separated from each other by a large distance, there is no interaction between them and the potential energy of the system is conventionally taken as zero. As the two hydrogen atoms approach each other, potential energy gradually decreases as is shown in Fig. 22.8. The essential condition for such energy lowering is, that the two electrons belonging to two hydrogen nuclei must have opposite or antiparallel spins. The lowering of energy becomes maximum when the two hydrogen nuclei are at a distance of r_0 from each other. If these are forced even closer than r_0, then coulmbic repulsion between the two hydrogen nuclei comes into play and thus proton-proton repulsion, being very strong, increases the energy of the system sharply and the system becomes highly unstable. Thus, when two hydrogen nuclei are situated at a distance of r_0 from each other, the energy of system is minimum. This state thus represents the hydrogen molecule, with r_0 being the length of the H—H bond.

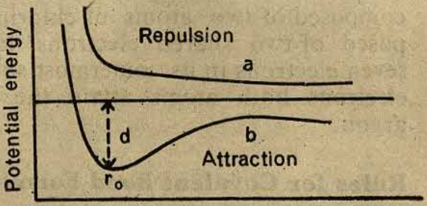


Fig. 22.8. Internuclear charge (Å)

It has been observed that helium does not form He_2 molecule. The reason is that when two helium atoms approach each other, repulsive forces overcome the attractive forces and therefore the individual atoms of helium can not come close together to form a bond. The formation of helium molecule is also not feasible energetically. The repulsive forces are stronger than the attractive forces. The energy of the system on the approach of two helium atoms, therefore, increases and hence bond formation is not possible.

22.11. MOLECULAR ORBITAL THEORY

Any molecule is supposed to have orbitals associated with it in much the same way as a single atom has. Just as each electron in a single atom can be represented by a wave function, ψ, denoting a particular atomic orbital, so each electron in a molecule can be represented by similar wave functions denoting particular molecular orbitals.

The various molecular orbitals associated with a molecule have different energy values and may have different shapes. They serve the same purpose as atomic orbitals in giving, through ψ^2 values, the relative probable electron densities in space. The Pauli principle applies to the molecular orbitals as to the atomic orbitals, so that no single molecular orbitals can contain two precisely similar electrons. This means that any particular molecular orbital can only contain two electrons with opposed spins.

The electrons associated with a molecule, excepting those in the inner shells of the atoms concerned, enter into molecular orbitals formation and these orbitals fill according to the energy and spin considerations. The essential difference between an atomic orbital and a molecular orbital is that an electron in the former is influenced by only one positive nucleus, whereas an electron in the latter is influenced by two or more nuclei. Thus one can assume that molecular and atomic orbitals have much in common and both seek to describe the nature of an electron within a nuclear field.

The most convenient way of working out the wave functions for molecular orbitals is to adopt LCAO (linear combination of atomic orbitals) MO method. This is an approximate method and is used

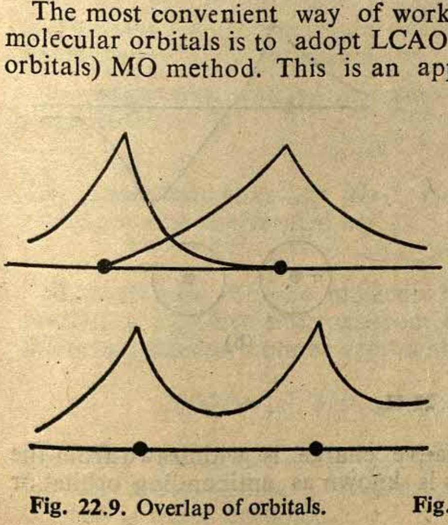


Fig. 22.9. Overlap of orbitals.

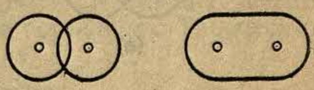


Fig. 22.10. Formation of covalent bond.

because the exact equations can not be solved. Let us consider the wave functions associated with

$$\overset{\circ}{A} \qquad \overset{\circ}{B}$$

$$\psi_A \qquad \psi_B$$

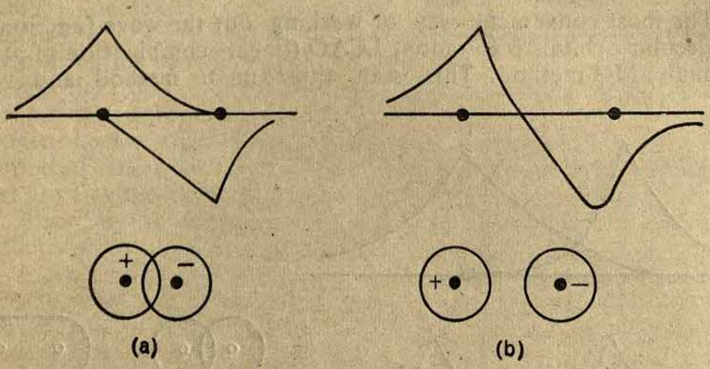
the atoms *A* and *B*. The molecular orbital wave function can be written as

$$\psi=\psi_A \pm \lambda\, \psi_B$$

can be obtained by the combination of atomic wave functions ψ_A and ψ_B. λ gives a measure of ionic character of the bond between *A* and *B* and its value is dependent on the nature of *A* and *B*. ψ_A and ψ_B are equal for a diatomic molecule and the value of λ is 1.

A combination of two similar atomic orbitals as in H_2 molecule gives the molecular orbital as shown in their curves shown in Fig. 22.9. The ψ-γ curves for the σ is molecular orbital, formed by combination of the two ψ-γ curves for 1*s* atomic orbitals. The boundary surface of the resulting molecular orbital is shown as below. As can be seen from here that there is an accumulation of negative charge between the nuclei. This holds the nuclei together at an equilibrium internuclear distance. The molecular orbital is called bonding orbital or σ Is orbital, σ because it is symmetrical about the molecular axis, 1*s* because it is formed by the combination of 1*s* atomic orbitals. The bond formed between two atoms by a σ-molecular orbital is called a σ-bond.

The combination of two similar 1s atomic orbitals by subtraction is most easily brought about after charging the sign of one of them as shown below



(a) (b)

Fig. 22.11.

The ψ-γ curves show that negative charge is withdrawn from the region between the nuclei. This is known as antibonding orbital or σ*1*s*.

A combination of two atomic orbitals must give two molecular orbitals to accommodate the available electrons. Each atomic orbital and each molecular orbital can contain two electrons with opposed spins. One of the molecular orbital is bonding orbital, the other is antibonding as shown in Fig. 22.12. A molecular orbital that concentrates electron density in the region between the nuclei is called a bonding molecular orbital. The spatial-boundary picture of a molecular orbital, like that of an atomic orbital, outlines the volume that encloses most of the electron density and consequently has a shape given by molecular wave function.

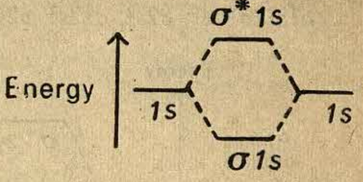


Fig. 22.12. Molecular orbitals for H_2 molecule.

The order of energy of molecular orbitals has been determined mainly from spectroscopic data. In homonuclear diatomic molecules the order is

$$\sigma 1s,\ \sigma^* 1s,\ \sigma 2s,\ \sigma^* 2s,\ \sigma 2p_x,\ \begin{cases}\pi 2p_y\\ \pi 2p_z,\end{cases} \begin{cases}\pi^* 2p_y\\ \pi^* 2p_z,\end{cases} \sigma^* 2p_x$$

$\longrightarrow$ increasing energy.

Electronic Structure of Molecules

The electronic structure of molecules can be written on the basis of Aufbau or build-up principle. The electrons are fed into atomic orbitals the ones having the lowest energy are filled up first. Each molecular orbital can accommodate a maximum of two electrons of opposite spins. In case there are number of molecular orbitals of the same energy (*i.e.* degenerate orbitals), Hund's rule is applied to decide the order of their filling up.

H_2 molecule. The H_2 molecule has two electrons which may be represented as

$$\sigma\ 1s^2$$

He_2^+ molecule ion. The He_2^+ molecule ion has three electrons which may be represented as

$$\sigma\ 1s^2,\ \sigma^*\ 1s^1$$

B_2 molecule. The B_2 molecule has total number of 10 electrons in molecule *i.e.* five electrons from each boron atom. The electronic molecular structure can be represented as

$$\sigma 1s^2,\ \sigma^* 1s^2,\ \sigma 2s^2,\ \sigma^* 2s^2,\ \begin{cases}\pi 2py^1\\ \pi 2pz^1\end{cases}$$

Since $\pi 2p$ orbitals are lower in energy than $\sigma 2px$ and $\pi 2py$ and $\pi 2pz$ orbitals are degenerate, according to Hund's rule each molecular orbitals is singly occupied.

N_2 molecule. In the N_2 molecule there are fourteen electrons distributed as under:

$$\sigma 1s^2,\ \sigma^*1s^2,\ \sigma 2s^2,\ \sigma^*2s^2,\ \sigma 2px^2 \begin{cases} \pi 2py^2 \\ \pi 2pz^2 \end{cases}$$

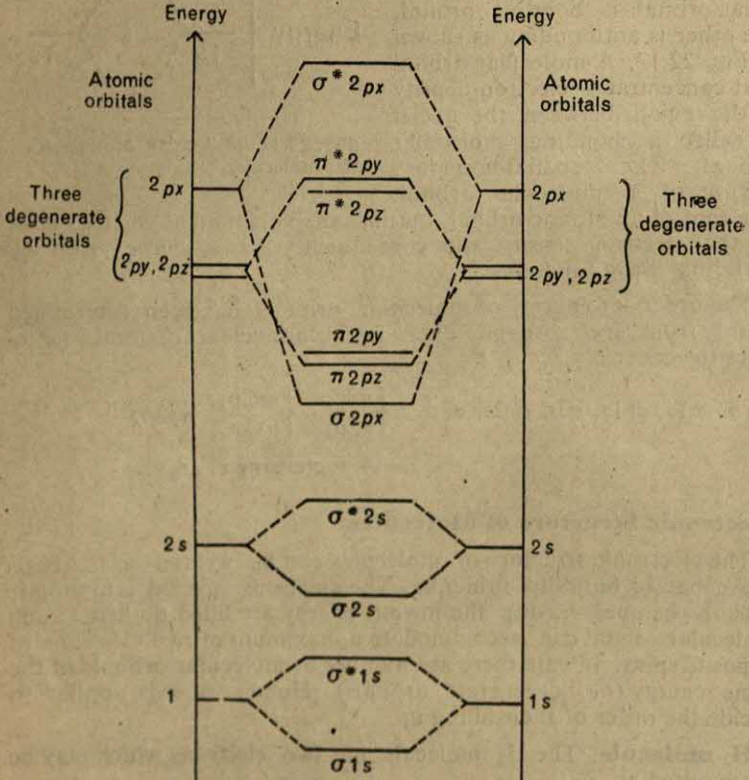


Fig. 22.13. Energy pattern for homonuclear diatomic molecules.

Here one sigma ($\sigma 2px$) and two pi bonding pairs participate in the bond formation. This is in agreement with the bond formation as N≡N. Since there are no unpaired electrons in the molecule, N_2 is diamagnetic in character.

O_2 molecule. In the O_2 molecule there are sixteen electrons which may be represented as

$$\sigma 1s^2,\ \sigma^*1s^2,\ \sigma 2s^2,\ \sigma^*2s^2,\ \sigma 2px^2, \begin{cases} \pi 2py^2 \\ \pi 2pz^2, \end{cases} \begin{cases} \pi^*2py^1 \\ \pi^*2pz^1 \end{cases}$$

This is because there are two unpaired electrons.

22.12. BOND ORDER

The term bond order is used to express the multiplicity of the link between two atoms. It is used in several different ways and its precise meaning should be deduced from the connotation. When used in connection with molecular orbitals of diatomic molecules the bond order is the number of pairs of electrons having a resultant bonding effect. This is shown in Table 22.5.

TABLE 22.5

Example of bond order is applied to molecules orbitals

	Number of electrons		
	in bonding orbitals	*in antibonding arbitals*	*Bond order*
H_2	2	0	1
H_2^+	1	0	1/2
He_2	2	2	0
O_2	8	4	2
O_2^+	8	3	2½
F_2	8	6	1

When used in connection with directed valence, bond order gives by information about the number of bonds which make up the link between two atoms. The total bond order is the total number of bonds between the atoms; the term mobile bond order stands for the number of bonds between the atoms. Thus the total bond order in ethylene $C=C$ is 2 and the mobile bond order is 1. In acetylene the total bond order is 3 and mobile bond order is 2. In conjugated systems the bond orders are usually fractional and the fraction has to be calculated from a knowledge of the conjugated structure. It has been found that as the bond length between two carbon atoms decreases, the bond order increases. This is shown in Table 22.6.

TABLE 22.2

Bond length and bond order (on MO theory)

Substance	*Bond length*	*Bond order*
Ethane	1.54	1.00
Graphite	1.42	1.53
Benzene	1.39	1.667
Ethylene	1.34	2 00
Actylene	1.20	3.00

22.13. VALENCE BOND METHOD

The valence bond theory describes the covalent bond and covalent bonding in molecules and complex ions in a quantitative manner. It places emphasis on the overlapping of atomic orbitals in the formation of bond. According to this theory, each atom uses electrons in one or more of its valence shell orbitals to form the covalent bonds.

According to this method the position of an electron in a molecule are adequately described by atomic orbitals. This method can best be illustrated by considering the example of hydrogen molecule.

The hydrogen molecule is composed of two protons H_1 and H_2 and two electrons e_1 and e_2.

In order to describe this molecule, it is assumed that e_1 occupies the ls orbital of hydrogen atom 1 and e_2 occupies the ls orbital of hydrogen atom 2. Let the ls orbital of hydrogen atom 1 be designated by S_1 and the ls orbital of hydrogen atom 2 as S_2. The function ψ_1, describes the positions of these two electrons in structure I of Fig. 22.14 is given by

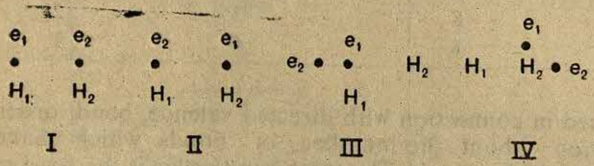


Fig. 22.14. The four possible structures for the hydrogen molecules.

$$\psi_1 = S_1(1)\, S_2(2)$$

where the symbol S_1 (1) refers to the fact that e_1 is the orbital S_1. ψ_1 represents the orbitals of both the electrons and that such a two-electron function is formed as the product of the one-electron functions. Another possibility of the structure is II where the electrons are exchanged, the position of the electrons

$$\psi_2 = S_1(2)\, S_2(1)$$

These two representations are equally probable.

A better picture can therefore be obtained by taking into account both structures I and II. The function ψ that describes the positions of two electrons is then formed as a linear combination of ψ_1 and ψ_2

$$\begin{aligned}\psi &= a_1\psi_1 + a_2\psi_2 \\ &= a_1[S_1(1)S_2(2)] + a_2[S_1(2)S_2(1)]\end{aligned}$$

Thus this wave function describes the two electrons in the covalent structure

$$H_1 - H_2$$

However a still better picture can be obtained if we take into account structures III and IV *i.e.*

$$\psi_3 = S_1(1)\,S_1(2)$$
$$\psi_4 = S_2(1)\,S_2(2)$$

The new function for the hydrogen molecule can be described as a linear combination of the four functions ψ_1, ψ_2, ψ_3, ψ_4

$$\psi = a_1\psi_1 + a_2\psi_2 + a_3\psi_3 + a_4\psi_4$$

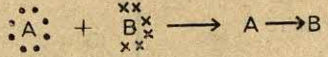
On solving the Schrodinger equation with this value of the wave function, the energy of bond formation for hydrogen molecule comes to be -92 kcal/mol. This is in good agreement with the experimental value of -109.6 kcal/mol.

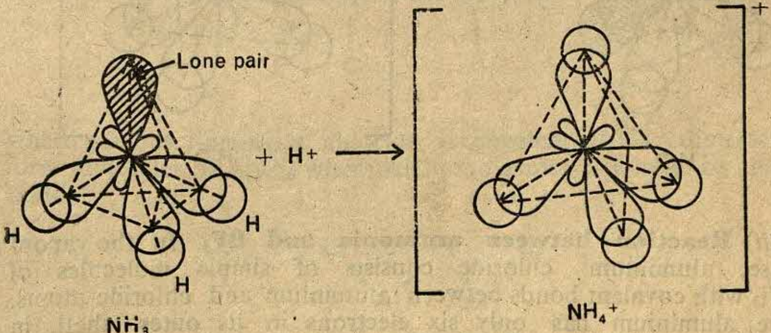
22.14. COORDINATE OR DATIVE BOND

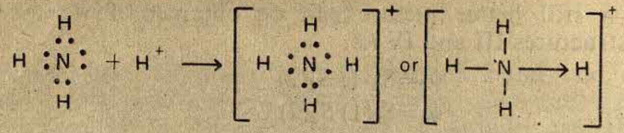
In a covalent bond, one electron is contributed by each bonded atom to a shared electron pair. In some cases both electrons in a covalent bond are supplied by one of the bonded atoms. This is called coordinate or dative bond.

According to the orbital theory a coordinate covalent bond results when an orbital containing a lone pair of electrons in one atom overlaps with an empty orbital present in the other atom.

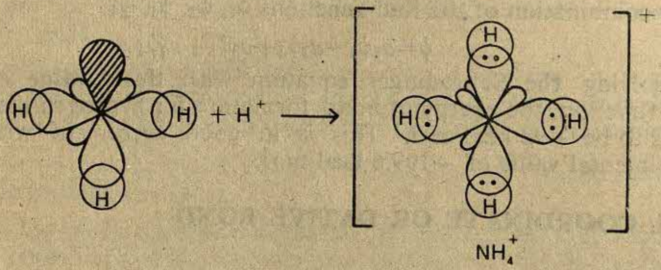
The atom sharing the pair of electrons from the donor is called the acceptor. The sign from the donor to acceptor signifies a coordinate bond and the process of forming a coordinate bond is called coordination. It is important to note note that the coordinate covalent bond once forced is indistinguishable from a covalent bond. A coordinate bond may be represented as







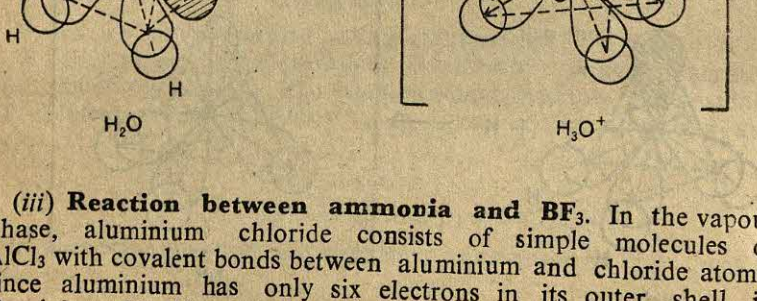
$$\mathrm{H{:}\overset{H}{\underset{H}{N}}{:}} + H^+ \longrightarrow \left[\mathrm{H{:}\overset{H}{\underset{H}{N}}{:}H}\right]^+ \text{ or } \left[\mathrm{H{-}\overset{H}{\underset{H}{N}}{\longrightarrow}H}\right]^+$$



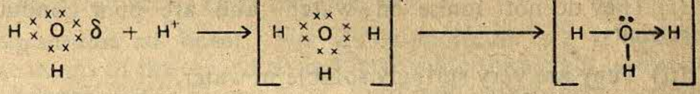
Examples of Coordinate Bond

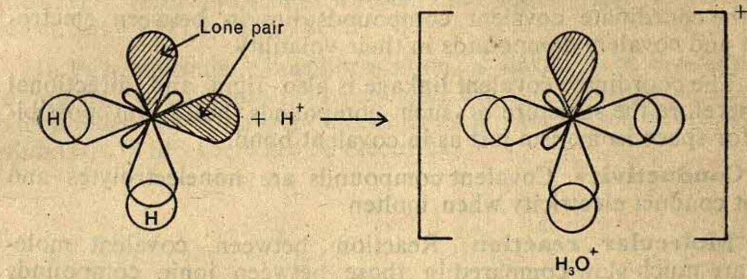
(*i*) **Formation of ammonium ion.** Ammonia molecule which has a lone pair of electrons can react with a hydrogen ion, H^+, having a vacant s-orbital by donating the lone-pair to H^+, whereby the H^+ attains its helium duplet, the NH_3 molecule, with one lone pair is called a donor, and the H^+ which receives the lone pair is termed an acceptor.

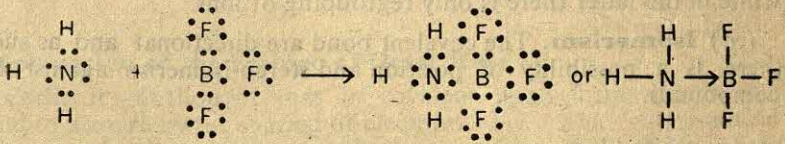
(*ii*) **Formation of hydronium ion.** In water there are two lone pairs of electrons. A hydrogen atom loses its solitary electrons to form a hydrogen ion



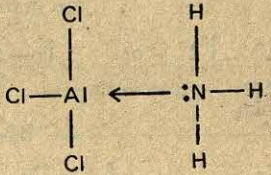
(*iii*) **Reaction between ammonia and BF$_3$.** In the vapour phase, aluminium chloride consists of simple molecules of $AlCl_3$ with covalent bonds between aluminium and chloride atoms. Since aluminium has only six electrons in its outer shell in aluminium chloride, two short of the noble gas structure for neon.



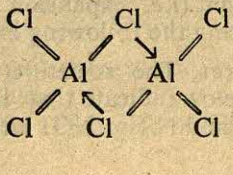




Nitrogen in ammonia has eight electrons in the outermost shell but two of these electrons are not shared with any other atom. When ammonia gas and aluminium chloride vapor are mixed they react rapidly to form the solid $NH_3.AlCl_3$. In this compound, the NH_3 and $AlCl_3$ have formed a bond because the N atom in NH_3 can denote a unsheared pair of electrons towards the Al atom. Thus completing its octet



where gaseous aluminium chloride is covalent, $AlCl_3$ dimerses to form molecules of Al_2Cl_6 where $AlCl_3$ molecules are held by dative bond



Characteristics of Coordinate Bond

(*i*) They do not ionise in water and are poor conductors of electricity.

(*ii*) They are very springly soluble in water.

(*iii*) Since coordinate linkage results in semipolarity, in the molecule, the coordinate covalent compounds lies in between electrovalent and covalent compounds in their volatility.

(*iv*) The coordinate covalent linkage is also rigid and directional and therefore the structure of such compounds holds out possibilities for space isomerism just as in covalent bond.

(*v*) **Conductivity**. Covalent compounds are nonelectrolytes and do not conduct electricity when molten.

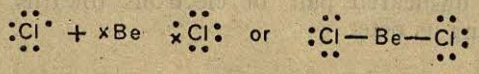
(*vi*) **Molecular reaction**. Reaction between covalent molecules are much slow compared in those between ionic compounds because the former involves the breaking and reforming the bonds, while in the latter there is only regrouping of ions.

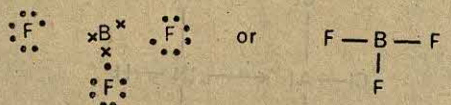
(*vii*) **Isomerism**. The covalent bond are directional and as such there is a possibility of position and stereo-isomerism against the compounds.

Types of Covalent Bonds

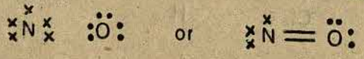
Covalent bond may be single, double or triple covalent bond. The latter two bonds are called multiple covalent bonds.

Single covalent bonds are formed by sharing only one electron pair between the bonded atoms *e.g.*





BF$_3$ Molecule



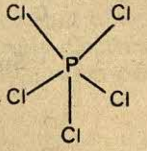
22.15. DEVIATION FROM OCTET RULE

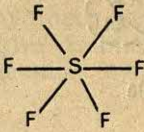
There are examples of molecules in which the octet rule breaks down *i.e.* atoms have electrons either less than eight (*i.e.* incomplete octet) or more than eight (*i.e.* expansion of octet). This fact can be illustrated by considering the following examples.

(*i*) **Incomplete octet**. The structure of $BeCl_2$, BF_3 and NO^- molecules as shown below indicate that the central atom viz., Be (in $BeCl_2$), B (in BF_3) and N (in NO) are surrounded by four, six and seven electrons in their valence shell respectively while other atoms of these molecules obey the octet rule.

(*ii*) **Expansion of octet**. No stable molecule are known in which the atoms of the second period have more than eight electrons in their valence shell. Elements of third and subsequent periods however, form molecules wherein the atoms have more than 8 electrons *e.g.* PCl_5, ClF_3, SF_6.

In PCl_5 molecule phosphorus atom is linked with five chlorine atoms by five covalent bonds, showing that the phosphorus atom is surrounded by $5+5=10$ electrons *e.g.* the octet is expanded. Similarly in SF_6 there are 12 electrons.





Explanation of the Failure of Octet Rule

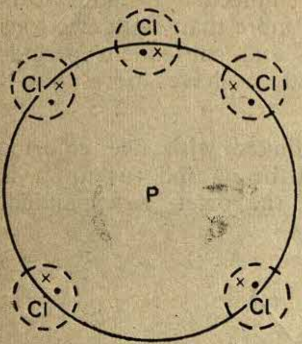
Earlier it was thought that in covalent bond formation, atoms tend to acquire by the sharing of electrons, the stable configuration of nearest inert gas. Consequently the outermost shell of an atom can not have more than 8 electrons. Sidgwick in 1933 pointed out that the covalency of an element may exceed four and the octet may be expanded. The maximum covalency of an element actually depends on the period in which the element concerned is present.

The maximum covalency of an element is limited according to the period in the periodic table, being 2 for hydrogen, 4 for the elements of second period, 6 for third and fourth and 8 for all the rest. The aforesaid, rule is known as Sidgwick covalency rule, may be expressed in the tabular form as:

Period	*Element*	*Atomic number*	*Maximum covalency shared pair of electrons*	
1	H	1	2	(4)
2	Li-F	3·9	4	(8)
3	Na-Cl	11-17	6	(12)
4	K-Br	19-35	6	(12)
5	Pb-I	37-53	8	(16)
6	Cs-At	55-85	8	(16)
7	Fr-onwards	87-onwards	8	(16)

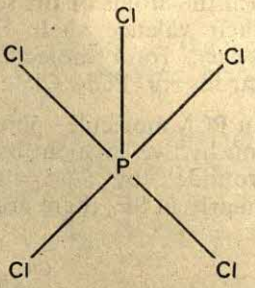
On the basis of Sidgwick's rule the structure of PCl_5 can be shown in Fig. given on the next page.

Sudgen's view of singlet linkage. Sudgen's however believes that octet rule is never violated and in PCl_5, the three chlorine atoms are linked with P-atom by three covalent bonds (*i.e.*



Electronic formula

or



Structural formula

three electropairs are being shared between P and Cl atoms) and each of the two remaining two Cl atoms is linked to P-atom by a bond formed by the sharing of only one electron between P- and Cl-atoms. This bond which is established by the one sided sharing of only one electron between two atoms is called singlet linkage.

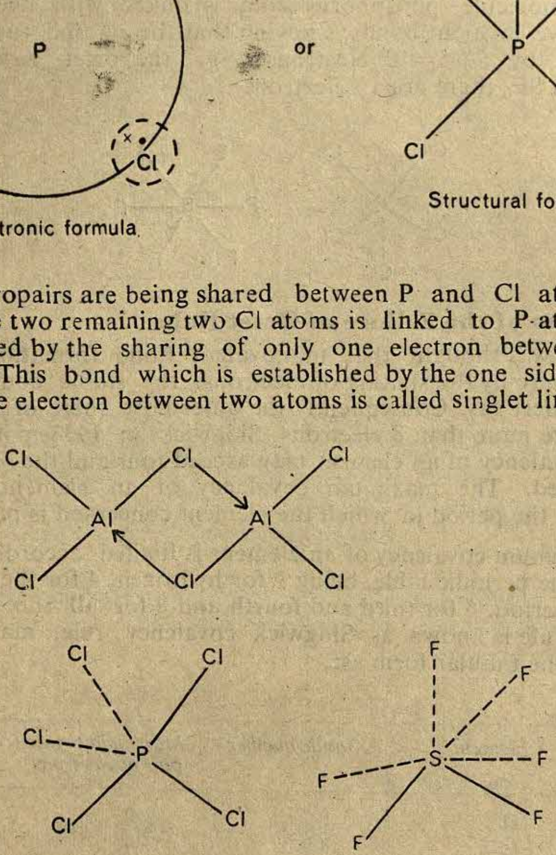


Fig. 22.15. Singlet linkage.

22.16. HYDROGEN BOND

When a hydrogen atom is bonded to a highly electronegative atom like fluorine, the electron-pair holding the two atoms together is displaced towards the electronegative fluorine atom, giving rise to the dipolar character in HF molecule:

$$H\!:\!\underset{\cdot\cdot}{\ddot{F}}\!:\,: \quad \text{or} \quad \overset{\delta+\,\delta-}{H-F}$$

Because of its 1s configuration hydrogen atom does not any screening electrons. As a result, in the HF molecule, a part of the positively charged nucleus (the proton) remains exposed and this residual positive charge attracts another electronegative fluorine atom of another HF molecule, the H-atom acting as bridge or bond between the two F-atoms which may be represented as,

$$\overset{\delta+}{H}-\overset{\delta-}{F}\ldots\ldots\overset{\delta+}{H}-\overset{\delta-}{F}$$

and this type of bonding is known as hydrogen bond. Thus, hydrogen bond may be defined as the electrostatic force of attraction which holds two polar molecules together through the mediation of a hydrogen atom covalently bonded to an electronegative atom. It can also be defined as:

The attractive force that binds a hydrogen atom which is already attached with a strongly electronegative atom of a molecule with another electronegative atom of some other molecule is known as hydrogen bond.

Types of Hydrogen Bonding

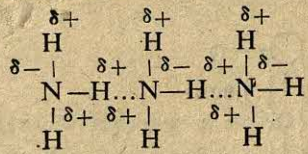
Hydrogen bond has been divided into two major classes.

(*ii*) **Intermolecular hydrogen bond**. The hydrogen occurring between two or more similar or different molecules is called intermolecular hydrogen bonding.

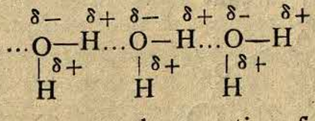
Examples of hydrogen bonding. When a number of HF molecules are brought together, the positive end of one dipole $\overset{\delta+}{H}-\overset{\delta-}{F}$ attracts the negative end of the other similar dipole $\overset{\delta+}{H}-\overset{\delta-}{F}$ and these molecules are associated together to form a cluster $(HF)_n$

$$\ldots\overset{\delta+}{H}-\overset{\delta-}{F}\ldots\ldots\overset{\delta+}{H}-\overset{\delta-}{F}\ldots\ldots\overset{\delta+}{H}-\overset{\delta-}{F}$$

Other examples are water and ammonia



$$\begin{array}{cccccccc} & \overset{\delta+}{H} & & & \overset{\delta+}{H} & & & \overset{\delta+}{H} \\ \delta- & | & & \delta+ & |\,\delta- & & \delta+ & |\,\delta- \\ & N & - & H\ldots & N & -H\ldots & & N-H \\ & |\,\delta+ & & \delta+ & | & & \delta+ & | \\ & H & & & H & & & H \end{array}$$

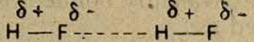


$$\begin{array}{l} \ldots\overset{\delta-}{O}-\overset{\delta+}{H}\ldots\overset{\delta-}{O}-\overset{\delta+}{H}\ldots\overset{\delta-}{O}-\overset{\delta+}{H} \\ \quad |\,\delta+ \qquad\quad |\,\delta+ \qquad\quad |\,\delta+ \\ \quad H \qquad\qquad H \qquad\qquad H \end{array}$$

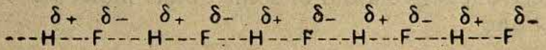
The structure and properties of water and ice can be explained in terms of hydrogen bonding. The unexpectedly high values for melting point, boiling point, molar heats of vaporisation and fusion are due to the formation of H-bond. This extra bonding between H_2O molecules also causes high surface tension and high viscosity. Because of high surface tension of water which provides a sort of 'skin effect', it is possible for small but relatively dense particles such as razor blades and beetles to float on an undisturbed water surface.

The presence of two hydrogen atoms and two lone electron pairs in each water molecule results in a three dimensional tetrahedral structure in ice, (Fig. 22.16). Each oxygen atom in an ice is surrounded tetrahedral structure in ice. Each oxygen atom in ice is surrounded tetrahedrally by four others with hydrogen bonds linking each pair of oxygen atoms.

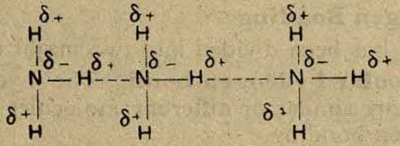
The distance between adjacent oxygen atoms is 0.276 nm, more than twice the O-H distance 0.096 nm in gaseous water molecules. This suggested that the hydrogen atom linking the two oxygen

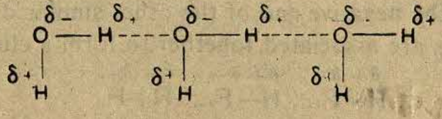


$$\overset{\delta+}{H}-\overset{\delta-}{F}------\overset{\delta+}{H}-\overset{\delta-}{F}$$



$$---\overset{\delta+}{H}---\overset{\delta-}{F}---\overset{\delta+}{H}---\overset{\delta-}{F}---\overset{\delta+}{H}---\overset{\delta-}{F}---\overset{\delta+}{H}---\overset{\delta-}{F}---\overset{\delta+}{H}---\overset{\delta-}{F}$$





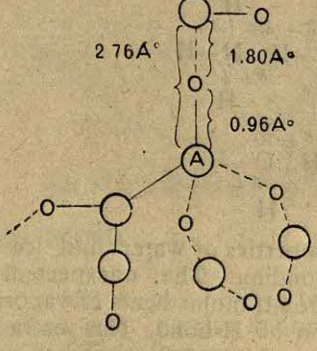
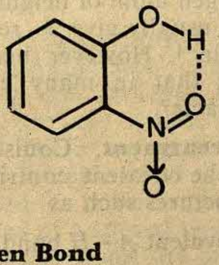


Fig. 22.16. Crystal structure of ice. The central oxygen atom, A is surrounded tetrahedrally by the oxygen atoms, 1, 2, 3, and 4. The ydrogen atoms are shown as small circles.

atoms in ice is probably not between them. The arrangement of water molecules in ice creates a very open structure which accounts for the fact that ice is less dense than water at 0°C. When ice melts, the regular lattice breaks up and the water molecules can pack more closely and so the liquid has a higher density. The anomalous physical properties have a staggering influence biologically and environmentally.

The fact that ice is less dense than water at 0°C means that ponds and lakes freeze from the surface downwards and the layer of ice insulates the water below presenting complete solidification. If ice were more than water, water would freeze from the bottom upwards and ponds would freeze completely killing fish, aquatic plants and other water living creatures. But for the hydrogen bonding, water would probably be a gas under normal atmospheric conditions, oceans, lakes and river would never exist and it would never rain.

(*ii*) **Intramolecular hydrogen bonding (chelation)**. Hydrogen bonding occurring within a single molecules is called intramolecular H-bonding. In intramolecular hydrogen bonding the H-atom is bonded to two atoms of the same molecules. This type of H-bonding may lead to the linking of two groups to form a ring structure and such an effect is one kind of chelation. For example 1, 2-substituted benzene compounds, 2-nitrophenol boils at 214°C as compared with 290°C for 3-nitrophenol and 279°C for 4-nitrophenol. Moreover 2-nitrophenol is more volatile in steam and less soluble in water than the other two isomers. 2-nitrophenol contains an internal hydrogen bond.



Properties of Hydrogen Bond

(*i*) Hydrogen bonds are noted between highly electronegative atoms such as fluorine, oxygen, chlorine and nitrogen.

(*ii*) Hydrogen bond is comparatively weak, their energies being only of the order of 5 kcal (6.7 kcal for FHF, 4.5 kcal for OHO, 1.3 kcal for NHN) as campared with roughly 100 kcal for ionic or covalent linkages.

(*iii*) Hydrogen bond is different than covalent bond because there is no sharing of electrons.

(*iv*) Hydrogen bond is formed more easily when both the atoms are highly electronegative. For example; the case of formation of a hydrogen bond in *A-H . . . B* increases with the increase in the electronegativity value of atom A represented as XA. This clearly explains that the tendency of A-H bond to form a hydrogen bond increases from N-H through O-H to F-H since XN, XO, XF.

Theories of Hydrogen Bonding

In order to explain the nature of hydrogen bonding various theories have been putforth, some of these are:

(*i*) **The electrostatic theory**. The fact that hydrogen bonding occurs only between very electronegative elements, suggests that electrostatic interaction between polar groups may be sufficient explanation.

Let us consider the covalent bond between hydrogen and some very electronegative atom A. The electron charge cloud between the two atoms will be considerably distorted to give a greater concentration of electron density in the vicinity of A and a strong dipole will be produced. A second electronegative atom B attached to another molecule or atom will also form negative end of dipole on $A—H$ and the negative charge on B will be greater than repulsive forces between like charges. The closer the B can approach H, the stronger will be this electrostatic link between them. The strength of the electrostatic attraction can be calculated approximately, by assuming a model in which the orbitals are represented by point charges at their controids. Lone pair of electrons play an important part in determining the strength and direction of hydrogen bonds. Calculations on the water molecule indicate that the strongest bond is formed when the $O—H$ axis of one molecule is co-linear with the lone pair axis on the oxygen atom of neighbouring water molecule. Calculations of this kind usually give a reasonable hydrogen bond energy of about 2 kJ mole^{-1}. However there are some objections to this theory, and it seems that in many cases hydrogen bond may have some covalent character.

(*ii*) **Valence bond treatment**. Coulson and Danielsson have attempted to determine the covalent contribution to the hydrogen bond by considering structures such as

$A—H$	covalent $A—H$ bond
$A^-H^+ \ldots B$	ionic $A—H$ bond
$A^-H—B^+$	covalent $H—B$ bond.

The calculations are necessarily approximate, and involve a considerable number of assumptions, but indicate that the covalent contribution may be appreciable, especially in 'short' hydrogen bonds.

(*ii*) **Molecular orbital treatment.** Pimentel has discussed hydrogen bonding in the HF_2 ion using molecular orbital theory. According to him, 1s, orbital of hydrogen atom combines with two 2p atomic orbitals of two fluorine atoms along the bond formation axis. Thus if the p orbitals of two fluorine atoms are denoted P and

P, the symmetrical $F—H\ldots F$ bond is described as

$$\psi_1 \text{ (bonding)} \quad = P_A + P_B + a_1 s$$
$$\psi_2 \text{ (non-bonding)} = P_A + P_B$$
$$\psi_3 \text{ (antibonding)} = P_A + P_B - a_3 s$$

where a_1 and a_3 are mixing coefficients. The two electrons involved in bond formation are contained in a molecular orbital (ψ_1) which spreads on either side of hydrogen atom, thus forming two equivalent weak bonds. Two electrons are concentrated mainly on the fluorine atoms in the non-bonding orbital ψ_2.

Application of Hydrogen Bonding

It can be realised that without hydrogen bonding, water would have existed as a gas like hydrogen sulphide. In that case, no life would have been possible on this globe.

Hydrogen bonding also exists in all living organism whether of animal or of vegetable kingdom. Thus it exists in various tissues, organs, blood, skin and bones in animal life. It also plays an important role in determining structure of proteins which are so essential for life. It also plays an important role in making wood fibres more rigid and thus makes it an article of great utility meet requirements of housing, furniture, etc. The cotton, silk or synthetic fibres owe their tensile strength to hydrogen bonding. Thus hydrogen bonding is thus a phenomenon of great importance in everyday life.

22.17. METALLIC BOND

Metals have some very characteristic properties. Each atom in the crystal has a very high coordination numbers (normally twelve and sometimes eight), and the structure has high electrical and thermal conductivity; they are very opaque and have high reflecting power *i.e.*, are lustrous. These are generally, hard, ductile and malleable. Metals have high melting and boiling points. Such properties cannot be accounted for in terms of normal ionic or covalent bonding hence that the idea of a special type of bond called metallic bond is necessary. Since metal atoms are packed together close to together in the crystal; this implies that there is extensive overlap of the outer electron orbitals and that the valence electrons can no longer be associated with a particular nucleus, but are completely delocalised over all the atoms in the structure together to fill space as completely as possible. There are two ways of 'close-packing' of identical spheres; one of these has haxagonal and the other cubic symmetry, but in each case the coordination number is twelve. The 'body-centred' cubic structure of the alkali metals is less closely packed and the coordination number in this case is eight.

Metals have very distinctive properties. In particular they are good electrical and thermal conductors; they are very opaque and have high reflecting power, *i.e.*, they are lustrous. Metals are generally hard, ductile and malleable; and have very high melting and boiling points, though the numerical range is wide. These crystallise in crystals with high coordination numbers of 12 or 14. Such properties of metals cannot be explained on the basis of normal ionic or covalent bonding. Since all the atoms of a metal crystal are identical these cannot be bound together in an ionic crystal. van der Waals forces are much too weak to account for high melting points of metals. Also each atom in a metal crystal cannot be bonded to each of its 8 or 14 neighbours by ordinary electrons is insufficient for the formation of covalent bonds with all the close or closest neighbours. Consider the case of lithium, it has one valence electron, the electronic configuration being 1s s. It is not possible for one lithium atom to get bonded to eight other atoms through covalent, *i.e.*, electrons pair bonds, as it contains only one valency electron. But it has 4 valency orbital (viz. 2s, 2p, 2py, 2pz) available. Hence besides its own valency electron, the valence electrons of the neighbouring atoms can also come quite close to its nucleus. In other words, there can be complete freedom of movement of electrons in the vacant valence orbitals around the nucleus of each lithium atom. The valence electrons of metallic atoms, thus are not localized at each atom. Metallic bond may be regarded as the one which tells as to how the metal atom in a metal crystal are bonded together. A brief account of theories of metallic bond is given below:

Electron Gas Theory

Drude in 1900 has developed this theory which was later modified by Lorentz (1916).

According to this theory each atom in a metal crystal looses all its valence electrons. The electrons thus obtained form an electron pool or gas. The resulting positively charged metal ions are believed to be held together by this electron pool or gas. The positively charged metal ions do not float randomly in the sea of electrons but have definite position at measurable distances from each other

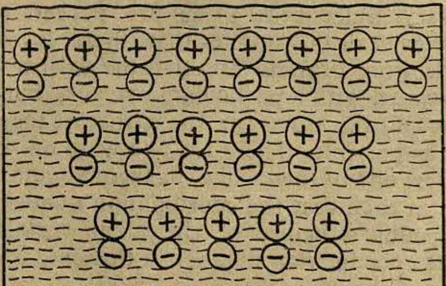


Fig. 22.17. Structure of metallic crystal.

in crystal a lattice. Since the valence-electrons are not attached to any individual ions or pairs of ions, but belong to the crystal as a whole, they are free to move throughout the lattice from one part of the crystal to the other as gas molecules move freely throughout the container. According to this theory, metallic solids may be regarded as a collection positive atomic cores immersed in a fluid of mobile electrons or sea of mobile electrons (see Fig. 22.17). Hence, the force that binds a metal atom to a number of electrons within its spheres of influence is known as metallic bond.

Valence Bond Theory

Pauling approach to the problem of binding in metals is essentially modified version of valence bond method that was used in explaining the concept of covalency. According to him, the structure of metals and alloys, may be described in terms of covalent bonds that resonate among alternate interatomic positions in the metals. Although the number of nearest neighbours of an atom in a metal exceeds its valence electrons. He postulates that resonance permit the existence of normal covalencies which resonate between all possible equivalent pairs For example potassium whose atom possess one valence electron crystallize into a body centred structure so that each atom has eight equivalent neighbours together with six other, close neighbours. Since each potassium atom has only one neighbour at one particular time, however, the concept of resonance permits the bonding electron pair to be considered as existing at first between one pair of atoms, and then another and another etc. Consequently the distribution of valence bonds, each containing an electron pair, may be represented for a crystal of potassium metal in the following structures: These structures indicate the possibililies of two bonds to one atom and none to another, which implies that the metallic bond possess characteristics of both ionic and covalent bonding. However, because of resonance variations it must be different from either. Furthermore, to account for the properties of a metal, the valence bonds must be considered as resonating at random among the various possible positions. Pauling regards potasssium atom as well as about three· forth of all other metal atoms as possessing an extra orbital in addition to those normally occupied by unshared or bonding electrons. The particular orbital is called the metallic orbital, and it plays a special role in metallic resonance. In the resonating structures for potassium metal one of the atom has formed two bonds by attaining the K^- configuration. To form the extra bond, this particular atom must be holding two electrons instead of one, as in normal atom. Therefore the atom designated as K^- must have an extra orbital available, and this is the so called metallic orbital.

K–K K K K –K
K–K K K K K

Molecular Orbital Theory

The delocalisation of free electron orbitals over all the atoms of a metal structure is, essentially, a molecular-orbital approach to metallic bonding. We know that when two atoms combine to form a diatomic molecule, two molecular orbitals are formed by the overlap of atomic orbitals of the combining atoms. When a third atom is added to the diatomic molecule, three molecular orbitals are obtained, and in general, when there is overlap of orbitals on N atoms in the solid structure, N molecular orbitals will be obtained. Now each orbital has an associated energy value and Figure illustrates diagrammatically the difference between the energy level of two orbitals of an isolated atoms and the large number of closely spaced levels which result from the overlapping of orbitals in a metal structure, The level become so close together in the metal that they effeetively form a band of energy values. These bands may be separated from each other so they may overlap. Each level can accommodate two electrons, so that, if there are N 'free' electrons, the first $N/2$ states will be doubly occupied.

Properties of Metals

(*i*) **Conduction phenomenon.** Metallic material in general show high electrical conductivity without material transfer and high thermal conductivity. Electrical conductivity is a periodic function of atomic numbers being highest (per atom) for univalent metals, less for divalent metals and at minimum values for multiple electron metals. In general it decreases with temperature and resultant increase in the frequencies of atomic vibrations.

(*ii*) **Optical properties**. Metals are uniformly lustrous and all but copper and gold are silvery of grayish. It is apparent, except copper and gold, that metals must absorb light of all frequencies and immediately radiate it.

(*iii*) **Mechanical characteristics**. Metals are characterised by such mechanical properties as ductivity, malleabillity and flow upon application of stress. Although there is little resistance for deformation, there is an ample evidence for existence of strong cohesive forces which resist the complete fracture of disruption of the object.

(*iv*) **Emission phenomena.** Many metals when exposed to radiation of short wavelength or when heated to sufficiently high temperature emit electrons. These are respectively, the phenomena of photoelectric and thermionic emission. In photoelectric emission, there is always a limiting or threshold frequency below which no emission occurs. It is evident, then that an electron must be given a certain minimum amount of energy before it can escape from the metal. Photoelectric emission is temperature-independent up to the point at which thermoionic emission begins. Above this temperature electrons are emitted as a result of thermal energy.

Structural characteristics. Unlike the solid non-metallic elements which are made up of aggregations of discreate molecules and are comparatively open and with low densities, metals possess close packed structures in which each atomic particle is associated with a number of close neighbours.

Although these are properties which are thought of as characterizing all metallic substances, it must be emphasized that there are many borderline cases where an element possess some metallic properties and some nonmetallic ones. For example, antimony, germanium and lithium.

According to Bernal a metallic bond should possess the following characteristics:

(*i*) Ability to act between identical metallic atoms and at the same time between widely metallic atoms.

(*ii*) Lack of direction, as shown by retention of properties in the liquid state, and a saturation is permitted large number of close neighbours

(*iii*) Equilibrium repulsive force which is atomic in nature.

(*iv*) Ability to permit electron transfer from atom to atom.

(*v*) Attractive force varying inversely as some high power of the internuclear distance.

Insulators. These are those materials in which valance electrons are bound tightly to their parent atom and hence require very large electric current to remove from the attraction of nuclei.

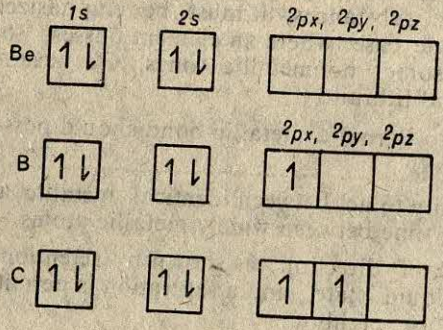
In terms of energy bands, an insulator has empty conduction band *i.e.* there are no electrons in this high energy band of the valence shell. The energy gap between valence shell band which is completely-filled (nonconduction band) and the conduction is very large. Thus energy required for shifting an electron band is very high and is therefore, not normally available. This explains that nonmetals are insulators.

22.18. HYBRIDISATION: (PROMOTION OF ELECTRONS)

The formation of bonds by overlap cf two atomic orbitals, requires that each of the two orbitals must contain one unpaired electron and that the two electrons must have different spins. This is because the molecular orbital formed by the overlap can only hold two electrons and they must have opposed spin by Pauli principle.

In this way, then, the number of bonds which an atom might be able to form depends to some extent, on the number of unpaired electrons in the atom. In terms of unpaired electrons, beryllium would be expected to behave as an inert gas, boron might be expected to be monovalent like fluorine, and corbon would be divalent like oxygen.

To meet the known chemical facts it must be assumed that some of the paired electrons are uncoupled or unpaired before the atom participates in chemical bonding. This will require an input of energy, but such energy will be available from the heat of reaction when covalent bonds are formed.



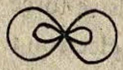


Fig. 22.18. Two co-linear *sp* orbitals.

The unpairing of electrons requires the removal of a 2*s* electron into a 2*p* orbital of higher energy level. This process is referred to as promotion is sometimes referred to as an excited valence state.

The excited state of beryllium, boron and carbon are as follows.

Such an excited valence states provide enough unpaired electrons for beryllium to form two, boron three and carbon four, bonds, but they are not the bonds, actually found in practice.

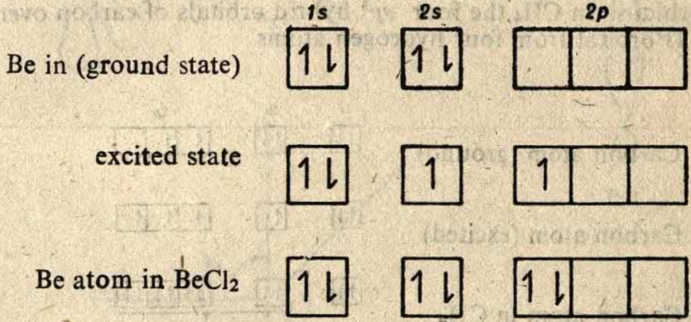
The excited structure given for carbon would give three bonds involving *p*-orbitals which would be right angles to each other together with a single bond involving an *s*-orbital. Methane, CH_4 for example would be expected by comparison with water and ammonia, to contain three *s-p* bonds mutually at right angles, and one weaker *s-s* bond. It is well established, however, that the four bonds in methane are all alike and are arranged tetrahedrally.

The answer to the problems posed at the end of the preceding section lies in concept of hybrid orbitals. This distinction between *s*- and *p*- and d-orbitals must be abandoned, so long as they have comparable energies, and it must be assumed that these orbitals can be combined in various ways within an atom to form different, but equivalent, hybrid orbitals. Such hybrid orbitals are more effective in forming strong bonds than 'pure' *s*, *p* and *d* orbitals.

The phenomenon of redistribution of energy in different orbitals belonging to the outermost energy level (valence shell) of an atom to give new orbitals of equivalent energy called hybridisation. The new orbitals thus formed are known as hybrid orbitals.

Sp (Linear or Diagonal) Hybridisation

The combination of an *s*- and *p*-orbital leads to two hybrid orbitals known as *sp* orbitals. The two *sp*-orbitals are colinear, when superimposed, as in Fig. 22.18. In beryllium chloride the two *sp* hybrid orbital of beryllium overlap two 3p-orbitals from two c lorine atom.



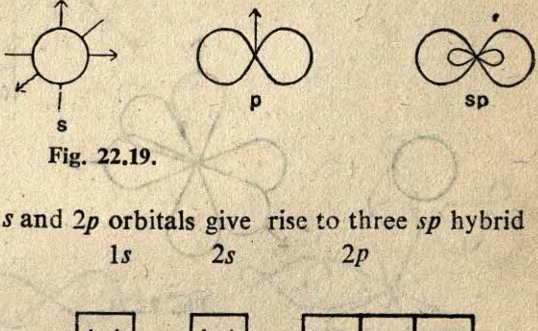
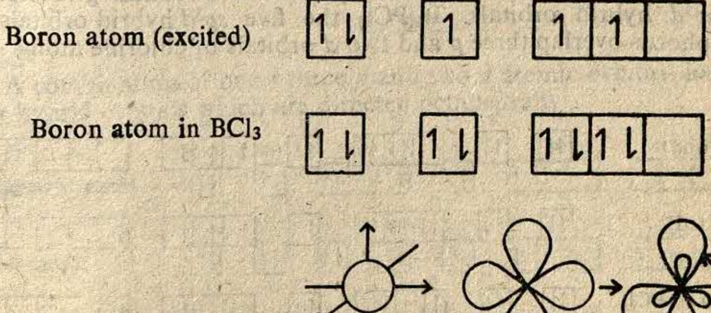


Fig. 22.19.

s-p^2 Hybridisation

The combination of 1*s* and 2*p* orbitals give rise to three *sp* hybrid



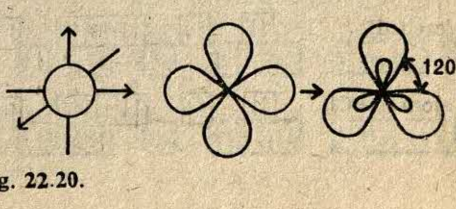
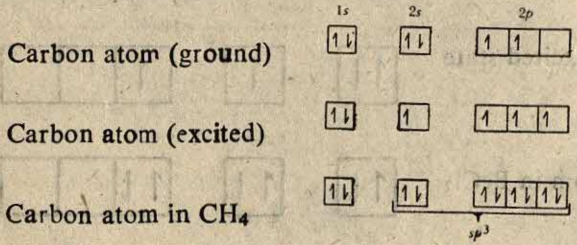


Fig. 22.20.

orbitals. In BCl_3, the three *sp* hybrid orbitals of boron overlap three 3*p* orbitals from chlorine atoms.

Sp^3 **Hybridisation**.

The combination of 1*s* and three *p* orbitals gives rise to four *sp*^{3} hybrid orbitals. In CH_4 the four *sp*^{3} hybrid orbitals of carbon overlap four 1*s* orbital from four hydrogen atoms



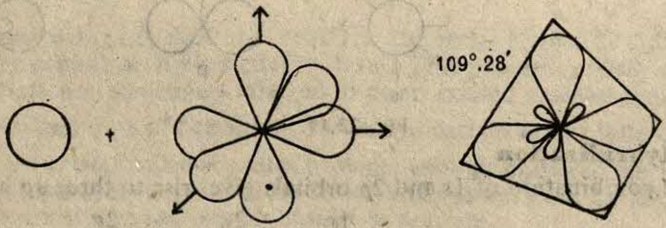
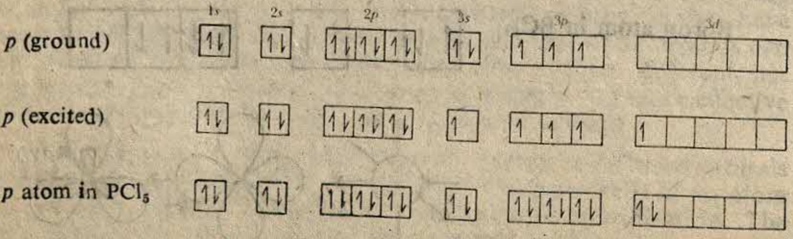


Fig. 22.21.

sp^3*d* (**Trigonal Bipyramidal**)

The combination of one *s*, three *p* and one *d* orbitals gives rise to five *sp*^{3}*d* hybrid orbitals. In PCl_5 the five *sp*^{3}*d* hybrid orbitals of phosphorus overlap three *p* and two *d* orbitals of chlorine atoms



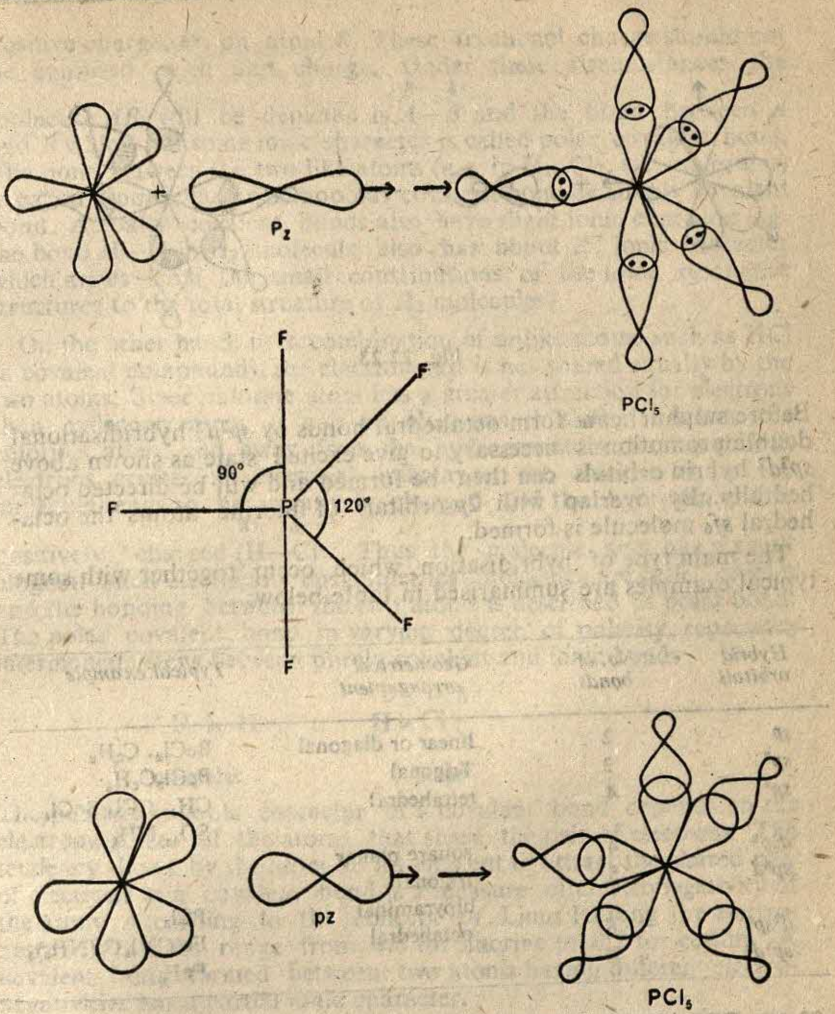


Fig. 22.22.

sp^3d^2

A combination of one *s* three *p* and two *d* atomic orbitals leads to six hybrid orbitals which are directed octahedrally

	1s	2s	2p	3s	3p	3d
S (ground state)	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑ ↑ ↑	
S (excited)	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	↑ ↑ ↑	↑ ↑
S atom in SF$_6$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓

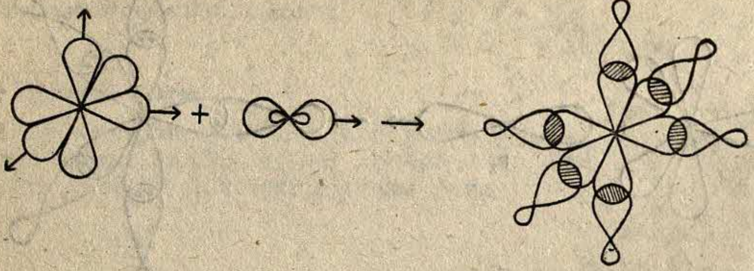


Fig. 22.23

Before sulphur can form octahedral bonds by sp^3d^2 hybridisational double promotion is necessary to give excited state as shown above sp^3d^2 hybrid orbitals can then be formed and will be directed octahedrally. By overlap with $2p$-orbitals of fluorine atoms the octahedral sf_6 molecule is formed.

The main type of hybridisation which occur together with some typical examples are summarised in table below:

Hybrid orbitals	*No. of bonds*	*Geometrical arrangement*	*Typical example*
sp	2	linear or diagonal	$BeCl_2$, C_2H_2
sp^2	3	Trigonal	$BeCl_3C_2H_4$
sp^3	4	tetrahedral	CH_4, CCl_4 $SnCl_4$ SO_4, NH_4
dsp^2	4	square planar	
sp^3d	5	trigonal bipyramidal	PCl_5
d^2sp^3	6	octahedral	$Fe(CN)_6Cr(NH_3)_6$
sp^3d^2	6	,,	FeF_6

22.19. POLARITY OF BONDS

As the shared electron pair between the atoms will necessarily be shared equally by both the atoms and hence the covalent bond will have no ionic character. Such type of bond may be regarded as true covalent bond. But in a covalent bond either between two unlike atoms *A* and *B* or between two like atoms having different neighbours the shared electron pair will not be equally shared by both the atoms, since if *A* atom has a stronger attraction for electron pair (*i.e.* has greater electron affinity) than *K*, the shared electron pair will be attracted towarns *A* away from *B*. This type of permanent displacement of electron pair towards *A* in the covalent bond will develop a fraction of negative charge δ^- on atom *A* and a fraction positive charge, δ^+, on atom *B*. These fractional charge should not be confused with unit charge. Under these circumstances the molecule *AB* will be depicted is $\overset{\delta-}{A}-\overset{\delta+}{B}$ and the bond between *A* and *B* which has some ionic character is called polar covalent bond. The bond between the two like atoms (*e.g.* in H_2, Cl_2, etc. molecules) is called a nonpolar or homopolar covalent bond or simply covalent bond. Actually covalent bonds also have slight ionic character *e.g.* the bond H—H in H_2 molecule also has about 2% ionic character which arises from the small contributions of the ionic resonance structures to the total structure of H_2 molecules.

On the other hand, in a combination of unlike atoms such as HCl (a covalent compound), the electron pair is not shared equally by the two atoms. Since chlorine atom has a greater attraction for electrons than hydrogen atom, a pair of electrons is shifted towards the chlorine atom and away from the hydrogen atom. Such a shift in electrons creates an electrical imbalance; the chlorine end of the molecule tends to be negatively charged and the hydrogen and is positively charged ($\overset{\delta+}{H}—\overset{\delta-}{Cl}$). Thus the molecule acts like a small magnet. Such electrically unsymmetrical molecules are called dipoles and the bonding between the two atoms is described as polar bond. The polar covalent bond in varying degree of polarity represents intermediate steps between purely covalent and ionic bonds

$$\underset{\text{nonpolar}}{\mathrm{H}\;\overset{\bullet}{\times}\;\mathrm{H}} \qquad\qquad \underset{\text{polar}}{\overset{\delta+}{\mathrm{H}}\,\overset{\bullet}{\times}\,\overset{\delta-}{\overset{..}{\underset{..}{\mathrm{Cl}}}}\,:}$$

The polarity or ionic character of a covalent bond depends on the electronegatives of the atoms that share the pair of electrons. The tendency shown by the atom of an element to attract the shared pair of electrons in a covalent bond is a measure of electronegativity of the atom. According to the concept of Linus Pauling the electronegativity values range from 4.0 for fluorine to 0·7 for cesium. A covalent bond formed between two atoms having different electronegativities has a partial ionic character.

22.20. SIGMA AND PI BONDS

An atomic orbital is a region in space near the nucleus of an atom in which there is a high probability of finding an electron. According to Pauli Exclusion Principle each electron in an isolated atom occupies a definite orbital and each orbital is capable of accommodating two electrons with opposite spins. If an orbital contains two electrons, they can not take part in chemical bonding unless unpairing occur first. However, a covalent, bond is set up due to overlap of atomic orbitals of the two combining atoms. The strength of a covalent bond is closely related to the extent of overlap of the atomic orbitals concerned.

When a single bond is formed between two atoms by overlap of orbitals along their axis (end to end overlap), the bond form is strong and is called sigma (σ-) bond. An overlap between two *s*-orbitals, an *s*-orbital and one lobe of *p*-orbital, or two lobes of two *p*-orbitals always gives rise a sigma bond, (Fig. 22.24).

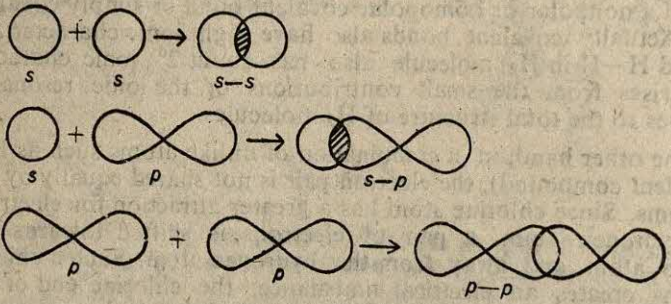


Fig. 22.24.

Because of the three dimensional character of the orbitals involved, rotation about a single eovalent bond is possible, rotation does not alter the degree of overlap of the orbitals involved. Bond of this type possessing axial symmetry are called σ-(sigma) bonds.

A double bond consists of a sigma bond and another type of bond called π (pi) bond. π-orbitals are usually formed by side to side overlap of *p* orbitals.

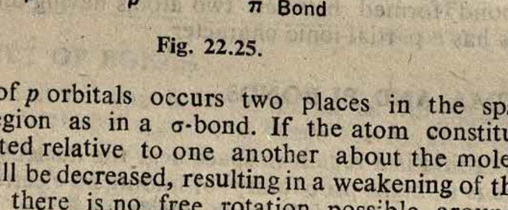


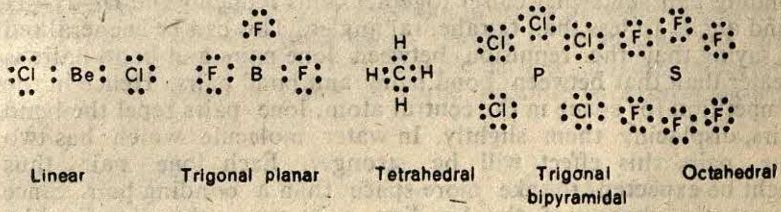
Fig. 22.25.

The overlap of *p* orbitals occurs two places in the space rather than single region as in a σ-bond. If the atom constituting the π bond are rotated relative to one another about the molecular axis, the overlap will be decreased, resulting in a weakening of the covalent bond. Hence, there is no free rotation possible around the bond axis of a π bond.

22.21. VALANCE SHELL ELECTRON PAIR REPULSION THEORY

Historically the spaces of many molecules were determined by organic chemists in the middle of 19th century. Recently such techniques as molecuar spectroscopy, X-ray, neutron and electron difraction and electron microscopy have confirmed these deduction and have provided precise information about molecular shape. As more knowledge about the molecular shapes developed it was realised that molecular shapes must result from orientation of the covalent bonds in different directions in space. It was argued that the shape was controlled by a 'central' atom bonded to two or more other atoms. The shape of a molecule can be predicted by valence shell electron pair repulsion VSEPR hypothesis and the application of valence bond theory.

The VSEPR method assumes that the electron pairs in the valence shell of a central atom take positions as for removed from each other as possible. This may be looked upon as repulsion between the electron pairs or as a consequence of the Pauli exclusion principle. The taking of different positions as far removed from each other as possible prescribes certain symmetric arrangements of the electron pairs. The particular arrangement depends upon the number of such pairs surrounding the central atom. To predict the shape of a molecule such as $BeCl_2$, BF_3, CH_4, PCl_5 and SF_6, write the electron dot formula. count the number of electron pairs, in the valence shell of the central atom and imagine these pairs to be oriented in space symmetrically. Thus $BeCl_2$ exists as linear molecule because two pairs of valence electrons on beryllium orient at 180° from one another and the two chlorines bond according to this orientation. Similarly BF_3, CH_4, PCl_5 and SF_6 will have trigonal plannar, tetrahedral. trigonal bipyramidal and octahedral respectively as shown in Fig. 22.26.



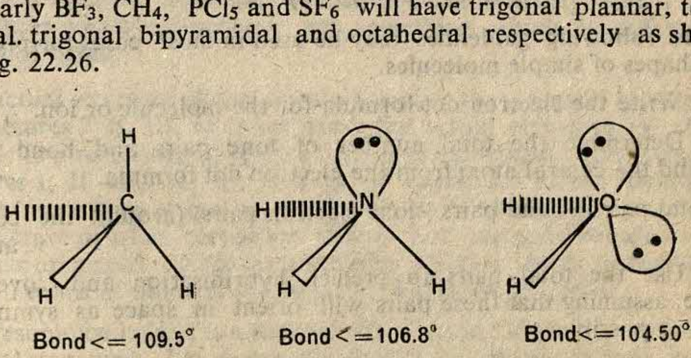


Fig. 22.26. The three molecules with lone pairs added showing the tetrahedral arrangement of the electron pairs.

The VSEPR method can also be used to predict the shapes of molecules in which one or more pairs of electrons in the valence shell of the central atom are not bonded to other atoms. Let us consider water and ammonia as an example

The central atoms in ammonia and water all contain four pairs. These four pairs should be arranged tetrahedrally around the central atom. From experiment the shape of ammonia molecule has been shown to be pyramidal and that of water to be bent. The bond angles for ammonia and water are not exactly tetrahedral as is the case in methane molecule. This may be explained from the observation that in methane all four electron pairs are bonded to hydrogen atoms *i.e.* in methane the four pairs are exactly equivalent. In ammonia, however, three pairs are equivalent and fourth in a lone pair. The lone pair not having a positive nucleus at the "other" end of the bond occupies more space on the nitrogen atom than a bonding pair. Due to electrostatic repulsion, it pushes the bonding pair somewhat closer together, thus reducing the H—N—H bond angles to less than tetrahedral angles. This can be generalised by saying that the repulsion between lone pairs and bond pairs is greater than that between bond pairs and bond pairs. Hence in the competition for space in the central atom, lone pairs repel the bond pairs, displacing them slightly. In water molecule which has two lone pairs this effect will be stronger. Each lone pair thus might be expected to take more space than a bonding pair. Since the negative charges of the bonding pairs are partly neutralised by the hydrogen nuclei, they might be expected to assume an arrangement requiring them to be closer together.

Thus according to the VSEPR hypothesis four pairs of electrons around a central atom will occupy approximately tetrahedral positions, but the exact symmetrical arrangement may be modified such that repulsion between bond pairs and bond pairs is less than repulsion between bonds pairs and lone pairs and this in turn is less than the repulsion between lone pairs and lone pairs *i.e.*

$$bp—bp \quad pb—1p \quad 1p—1p$$

The following guidelines may be used in most cases for predicting shapes of simple molecules.

1. Write the electron dot-formula for the molecule or ion.

2. Determine the total number of lone pairs and bond pairs around the central atom from the electron dot formula.

Total pairs=bond pairs+lone electron pairs (around the central atom).

3. Use the total pairs to predict hybridisation and "overall" shape, assuming that these pairs will orient in space as symmetrically as possible.

4. In describing the molecular shapes, relate the spatial positions of the atoms to a geometrical shape.

Problem. Predict the shape of F_2O

Solution. (*i*) Electron dot formula F O:F

(*ii*) Total pairs $=2+2=4$
(around the central atom)

(*iii*) sp^2 tetrahedral orientation

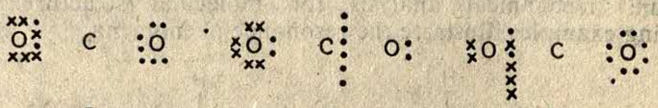
(*iv*) Shape is angular.

22.22. RESONANCE

There is, in fact, plenty of evidence that the actual chemical bonds occurring in chemical compounds are of a type intermediate between pure ionic and pure covalent bonds. A covalent bond may have some ionic character or a bond may be something in between a single and a double covalent bond.

The actual electronic arrangement in a compound which cannot be satisfactorily represented in one single structural formula using accepted symbols, had to be represented in terms of other possible, though non-existent structures which consist of a mixture of the various possible structures. For example carbon dioxide molecule can be represented in terms of three possible structures shown below:

$$O=C=O \qquad O\leftarrow C-O \qquad O\equiv C\rightarrow O$$



I II III

The actual structure of carbon dioxide which best accounts for all its properties would be something that is closely related to all the three possible structures, but something which is different from all of them.

The actual structure of the molecule is said to resonate between the structures I, II, III. In other words the actual structure of the molecule is a resonance hybrid of the three structures. The actual structures I, II and III are known as canonical forms. Various analogies have been suggested to facilitate the building up of a visual picture of what resonance means. For example rhinoceros, which has an actual existence, is thought of, as a sort of resonance hybrid in terms of unicorn and dragons, which do not exist.

The resonance hybrid is a more stable structure than any of the canonical structures. Let us consider that a resonance hybrid has two resonating structures I and II which have the wave functions

ψ_I and ψ_{II}. The suitable linear combination of these wave functions gives us third wave function which corresponds to a lower energy value; *i.e.*

$$\psi_{III} = N(C_I\, \psi_I + C_{II}\, \psi_{II})$$

The resonance energy of a substance may be defined as the extra-stability of the resonance hybrid as compared with the stable of the resonating structures as shown in Fig. 22.27.

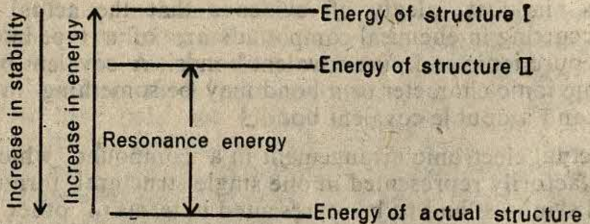
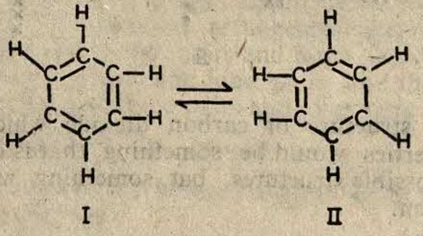
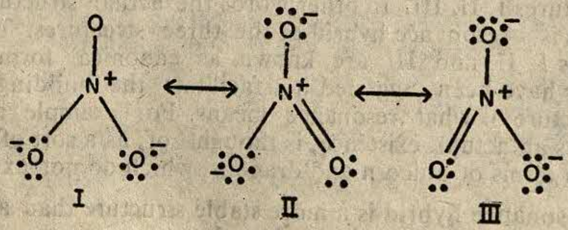


Fig. 22.27. Illustration of increased stability of the actual structure.

Examples of Resource

The method of combining two or more structural formulas to represent a single chemical species is called the resonance method. The method is used not only for the construction of electronic formulas but also as the basis of one method for doing approximate quantum mechanical analysis for molecular structure. The following examples illustrate the resonance phenomena.

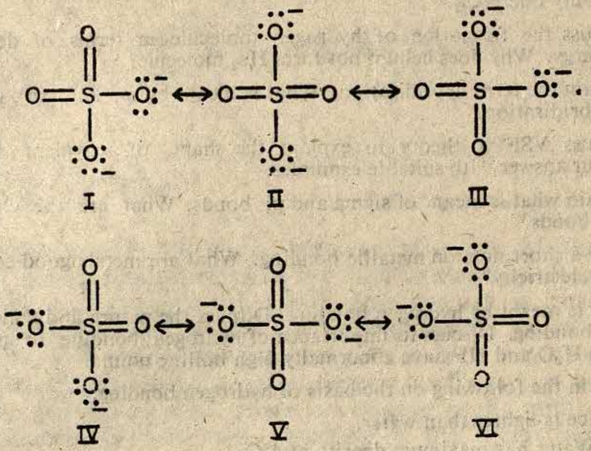




(*i*) Consider the benzene molecule which has six carbon atoms (C_6H_6) arranged in a ring, we can draw two resonance structures with alternate double bonds. However the structural studies reveal that all carbon-carbon bond distances are equal.

Nitrate ion has resonating structures shown on page 652.

The sulphate ion is a resonance hybrid of following six structures.



The resonance hybrid of six equivalent structure (I-VI) of $SO^{2}{}_{4}^{-}$ would have an average S-O bond order of 1½. The partial double bond order of S-O bond length has been confirmed by the actual observed bond length 1.49Å which 0.21Å shorter than the standard S-O single bond length of 1.70 Å which is obtained by adding the atomic radii of sulphur 1.04 Å and oxygen (0.66 Å).

PROBLEMS

1. What is chemical bond? When is a chemical bond formed between two atoms?

2. Why do atoms combine to form molecules? Give examples.

3. What do you understand about ionic bond? What are the conditions for the formation of an ionic bond?

4. What do you understand about covalent bond? Describe its conditions for the formation of covalent bond?

5. Give an account of electronic theory of valency. Explain clearly the difference between electrovalency, covalency and coordinate valency. How do covalent compounds differ from electrovalent compounds?

6. Write down the electronic formula of hydrogen chloride, magnesium chloride, hydrogen peroxide, hydrogen sulphide, carbon tetrachloride, sulphuric acid, boron trifluoride.

7. Explain variable electrovalency. Give examples.

8. Explain polarity of bonds with examples.

9. Discuss hybridisation and shape of the following molecules:

BF_2, CCl_4, PF_5, SP_6, IF_7

10. Give the geometry of the following compounds

NH_3, CH_4, H_2O, CF_4

11. Explain the following on the valency bond theory and hybridisation

(*a*) BeF_2 molecule in linear while SF_2 is angular.

(*b*) Phosphorus forms two chlorides PCl_3 and PCl_5 while nitrogen forms only one NCl_3.

12. Discuss the formation of hydrogen molecule in terms of decrease of potential energy. Why does helium not form He_2 molecule?

13. Explain the term hybridisation. What is meant by *sp*, sp^2, sp^3, sp^3d, sp^3d^2 and sp^3d^3 hybridisation?

14. Discuss VSEPR theory to explain the shape of covalent molecules. Illustrate your answer with suitable examples.

15. Explain what is meant of sigma and pi bonds. What are the characteristics of these bonds?

16. Wrire a short note on metallic bonding. What are metals good conductors of heat and electricity?

17. What is meant by hydrogen bonding? Dircuss the nature and consequences of hydrogen bonding. Discuss its importance of hydrogen bonding in substaining life. Why do H_2O and HF have abnormally high boiling points?

18. Explain the following on the basis of hydrogen bonding;

(*i*) Ice is lighter than water.

(*ii*) Water has maximum density at 4°C.

(*iii*) O chlorophenol is more volatile than *p*-chlorophenol.

(*iv*) O nitrophenol can be separated from *p*-nitrophenol by steam distillation.

19. What are the atomic and molecular orbitals? Based on the molecular orbital theory predict whether the following can exist (*i*) He_2 (*ii*) Li_2. Explain, why oxygen is paramagnetic and nitric oxide does not form dimer.

20. Discuss the bond properties of N_2, P_2, As_2 and Bi_2 in terms of their electronic structures.

21. (*a*) Derive by means of Born Haber-Cycle, the expression for the lattice energy of ionic crystals such as *MX* where *M* is a divalent metal and *X* is sulphur or oxygen.

(*b*) For MgO(s) $\Delta H_c = 931$ and $\Delta H_f = -145$ kcal mole^{-1}. Further for magnesium $\Delta H_s = 34$ kcal mole^{-1}, $I_1 = 7.64$ eV, and $I_2 = 15.03$ eV, while for $O_2(g)$ $\Delta H_d = 118$ kcal mole^{-}. Calculate from these data the electron affinity of oxygen.

Ans. $A = 170$ kcal mole^{-1}

22. Write short notes on the following:

(*a*) Resonance
(*b*) Bond energy
(*c*) Bond length
(*d*) Bond order
(*e*) Polarity of bond
(*f*) Sigma and Pi bonds
(*g*) Hybridisation
(*h*) Variable covalency
(*i*) Inert pair effect
(*j*) Octet rule
(*k*) Coordinate bond.

Chapter 23

NUCLEAR CHEMISTRY

23.1. INTRODUCTION

Nuclear Chemistry is concerned with the structure of the nucleus and how this structure influences the nuclear stability. It also deals with phenomena by means of which one nucleus is changed into another, such as the process of radioactivity and of nuclear transmutation. In ordinary chemical reactions, there is a rearrangement of the atomic electrons but the nuclei remain uneffected. On the other hand, in a nuclear reaction, there is a change in the number of protons or neutrons (or both) thus resulting in the formation of a new nuclei.

23.2. RADIOACTIVITY

In 1897, while investigating the phosphorescence produced in various materials by light, A.H. Becqueral discovered radioactivity. He had a pure sample of potassium uranyl sulphate, a crystal of this salt was placed on a photographic plate, wrapped in a black paper. Becquerel exposed the whole thing to sunlight. On developing the photographic plate, it was found to be darkened indicating that the uranium salt emitted radiations which could penetrate paper. He again repeated the experiment by keeping the uranium salt and the photographic plate wrapped in black paper, in a dark place. He found that the photographic plate was again exposed. From these observations Becquerel concluded that the radiations were emitted from uranium salt which affected the photographic plate and were capaple of passing through several layers of materials which were opaque to ordinary light. M. Curie, a student of Becquerel, found that the radioactivity of a given uranium compound was independent of the specific compound and that the quantity of radioactivity depended only on the quantity of uranium present. She further concluded that radioactivity is characteristic of certain elements rather than their compounds.

The radiations emitted by radioactive elements are heterogenous in character, and have been shown to consist of three types of radiations, *i.e.*, α, β, and γ-rays (see Fig. 23.1).

23.3. PROPERTIES OF α, β AND γ RAYS

Alpha rays. The nature of α rays was established by Rutherford's experiment. These consists of particles carrying 2 units of positive charge and a mass of 4 units. Thus the charge and mass of the alpha particles are identical with that of the helium nucleus.

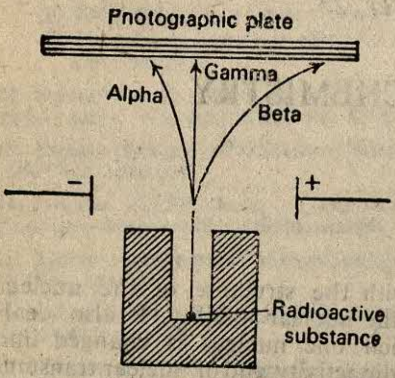


Fig. 23.1. Radioactive emissions.

When α-rays fall on a zinc sulphide screen, they cause phosphorescence (Fig. 23.2). The energies of α-particles range from 4 to 10 MeV and the velocities from 1.4×10^9 to 2.2×10^9 cm sec^{-1}. Owing to the large mass, the α-particles travel through gases in straight line and when pass through a gas cause its ionization. The actual path of α-particles through gases, has been photographed in Wilson's Cloud Chamber. In general the range of an α-particle varies approximately directly as the squareroot of atomic weight and inversely as the density of the medium through which it passes. They can penetrate through thin sheets of aluminium.

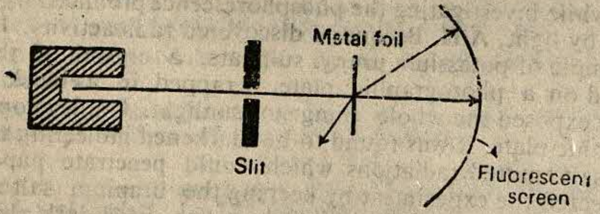


Fig. 23.2. Scattering of α-particles.

β-rays. A study of the behaviour of beta rays in the electric and magnetic fields shows that they consist of charged particles that are identical to electrons. Unlike α-particles, the β-particles do not have well defined energies. They travel through gases along much more erratic paths. The β-rays emitted by a given radioactive substance have a continuous distribution of energies, called the β-ray spectrum. β-rays are more penetrating than α-rays.

γ-rays. The gamma rays are not charged particles and hence are undeflected in electric or magnetic field. They are electromagnetic radiations of very short wave length, generally between 10^{-8} and 10^{-11} cm.

Gamma rays differ from X-rays in one very important aspect that γ-rays are of nuclear origin, whereas X-rays arise from energy changes involving electrons. γ-Rays are extremely penetrating, they can penetrate several centimetres thick lead sheets.

23.4. RADIOACTIVE DECAY

A nuclear species with a specific atomic number and a specific mass number is called a *nuclide*. For example $^{12}_{6}C$ is a nuclide with atomic number 6 and mass number 12. $^{14}_{6}C$ is an isotopic nuclide of $^{12}_{6}C$, both having the same atomic number but different mass numbers. The nuclides of $^{14}_{6}C$ and $^{14}_{7}N$ are not isotopic since they have same mass numbers but different atomic numbers. Such nuclides are known as isobars. On the other hand the nuclides $^{14}_{7}N$ and $^{15}_{8}O$ contain the same number of neutrons and are called isotones of each other.

The rate at which a sample containing radioactive nuclei emits particles does not depend on the chemical or physical state of the sample. Since radioactivity is a nuclear phenomenon, a radioactive nuclide will emit the same type of radiation at the same rate, regardless of the compound it is a part of, its temperature, the applied pressure, or the presence of electrostatic and magnetic or gravitational fields. The number of nuclei decaying per second is proportional to the number of nuclei present. Radioactive decay is a first order process and can be expressed by

$$-\frac{dN}{dt}=\lambda N \qquad \ldots (23.1)$$

where N is the number of nuclei remaining at any time t.

λ (lambda) is the proportionality constant, called the decay constant. The decay constant is a characteristic property of the given radioactive species.

Integrating the Equation (23.1), we get,

$$N=N_0\, e^{-\lambda t} \qquad \ldots (23.2)$$

where N_0 is the initial number of such atoms. Every radioactive species has a definite *half-life period*. It is the time required for the amount of a radioactive material to be reduced to half its initial value, so that the ratio N/N_0 is numerically equal to one half. The half-life period $t_{1/2}$ is given by

$$t_{1/2}=\frac{\ln 2}{\lambda}=\frac{0.693}{\lambda} \qquad \ldots (23.3)$$

Equation (23.3) shows that the time, needed for one-half of a quantity of radioactive substance to be disintegrated, is a constant, independent of the initial amount present and is characteristic of the given substance. Half-life period is a useful property for the identification of various nuclidic species.

The activity of a radioactive sample is defined as the number of disintegrations per unit time. The activity A is merely the rate of decay and is proportional to the number of atoms present that is:

$$A=\lambda N$$

The specific activity is defined as the number of disintegrations per unit time per gram of radioactive material. One *curie* is defined as an activity of 3.7×10^{10} disintegrations per second. The practical units are micro-curie (μ-curie) or milli-curie.

The half-life tells us how long it takes for half of the nuclei to decay while a related quantity, the mean life, τ, is the average time elapsed for dacay of an individual nucleus. It turns out the $\tau=\dfrac{1}{\lambda}$.

The measurement of half-life of an isotope helps in its identification. A detector is placed near the source of radiation and the number of particles striking the detector in a known short time interval are counted. This is shown in Fig. 23.3. The counting rate of the detector can thus be calculated which is proportional to the activity A of the source. The process is repeated after an elapsed time for decay. The resulting values of activity are plotted on semilog graph paper as shown in Fig. 23.4. A straight line is drawn

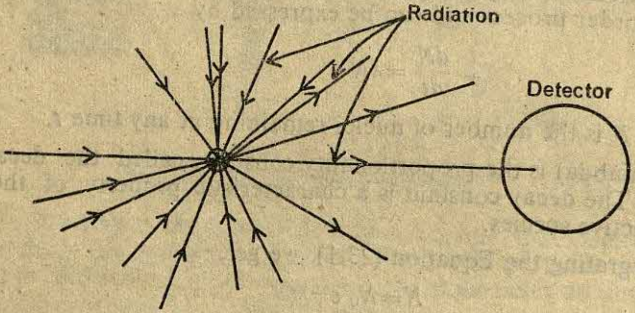


Fig. 23.3

through the observed points. From any pairs of point on the line λ and $t_{1/2}$ can be calculated. Activity plots can be used for a substance with very long half-life. However the measurement of activity of a radioactive substance is complicated by the presence of back ground radiation which is due to cosmic rays from outside the earth or from decay of minerals in the earth. It is always necessary to measure the background counts and subtract them from those observed in the experiment.

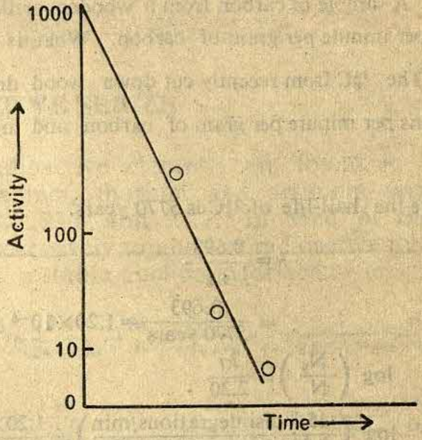


Fig. 23.4.

Problem. 23.1. Radium has atomic weight 226 and a half-life of 1600 years. Calculate the number of disintegrations produced from one gram of radium.

Solution. Half life period

$$t_{1/2}=\frac{0.693}{\lambda}$$

$$\therefore \qquad \lambda=\frac{0.693}{(1600)\ (365)\ (24)\ (60)\ (60)}$$

$$=1.38\times10^{-11}\ \text{sec}^{-1}$$

and

$$-\frac{dn}{dt}=\lambda N=\frac{(1.38\times10^{-11})(6.02\times10^{23})}{226}$$

$$=3.7\times10^{10}\ \text{disintegrations per sec.}$$

Radioactive dating. Isotopes of certain radioactive substances have long half-lives, they may be used in determining the age. Radioactive clocks (${}^{4}_{2}\text{He}$ from ${}^{238}_{92}\text{U}$, ${}^{87}_{38}\text{Sr}$ from ${}^{87}_{37}\text{Rb}$ and ${}^{208}_{82}\text{Pb}$ from ${}^{232}_{90}\text{Th}$) may be used for the purpose of dating. However the oldest terrestrial clocks are found to be 3×10^9 years old, and many meteorites are found to be about 4.5×10^9 years old. As soon as a plant or an animal dies, it ceases to take in any new carbon, because as C^{14} decays, the radioactivity of the carbon diminishes. W.F. Libby has shown on the assumption that since the intensity of cosmic radiation has not changed in the last several thousand years, a comparison of the activity of ${}^{14}C$ in a carbon derived from an ancient object with the activity of ${}^{14}C$ in "modern" carbon can be used to measure the age of that object. The method is known as "carbon dating." It is a most valuable tool in archaeology, permitting determination of the age (since its death).

Problem 23.2. A sample of carbon from a wooden artifact is found to give 7.00 $^{14}_{6}C$ counts per minute per gram of carbon. What is the approximate age of the artifact? The $^{14}_{6}C$ from recently cut down wood decays at the rate of 15.3 disintegrations per minute per gram of carbon and the half-life of $^{14}_{6}C$ is 5770 years.

Solution. Since the half-life of $^{14}_{6}C$ is 5770 years.

$$\therefore \qquad k=\frac{0.693}{t_{1/2}}$$

$$=\frac{0.693}{5770\text{ years}}=1.20\times10^{-4}\text{ year}^{-1}$$

$$\log\left(\frac{N_0}{N}\right)=\frac{kt}{2.30}$$

$$\log\left(\frac{15.3\text{ disintegrations/min}}{7.00\text{ disintegrations/min}}\right)=\frac{1.20\times10^{-4}\text{ year}^{-1}\ Xt}{2.30}$$

or

$$t=\frac{2.30\log 2.19}{1.20\times10^{-4}\text{ years}^{-1}}=6520\text{ years. Ans.}$$

23.5. GROUP DISPLACEMENT LAW

When a radioactive substance emits an alpha particle, it results in the production of an atom of a new element with an atomic number 2 units less and mass number less by 4 units than the parent atom. For example when a radium isotope of mass number 224 emits an alpha particle we have,

$$^{224}_{88}Ra \longrightarrow {}^{220}_{86}Rn + {}^{4}_{2}He.$$

On the other hand, the emission of a negative β-particle from a nucleus causes an increase in atomic number by 1 unit, but no change in the mass of the nucleus. We can consider the following example:

$$^{14}_{6}C \longrightarrow {}^{14}_{7}N + {}^{0}_{-1}\beta.$$

This information is embodied in the *group displacement law*, proposed independently by K. Fajan, A.S. Russel and F. Soddy. This Law may be stated as:

When an α-particle is emitted in a radioactive change, the product is displaced two places (or groups) to the left in the periodic table and the emission of a negative β particle results in a displacement of one place (or group) to the right. The law may be extended to include positive β-particle emitters and nuclei which exhibit orbital electron capture. This process is called K capture because an electron in the *ls* orbital (K shell) of an atom is most likely to be captured. K capture results in a decrease in atomic number but no change in mass number. We can consider the following example:

$$^{22}_{11}Na \longrightarrow ^{22}_{10}Ne + ^{0}_{+1}\beta$$

23.6. RADIOACTIVE SERIES

Three series of radioactive elements are found in nature. These are known as uranium, thorium and actinium series. These are shown in Figs. 23.5, 23.6, and 23.7. In each of these series, the elements decay successively to another radioactive nuclide until after a number of steps, a stable nuclide is formed.

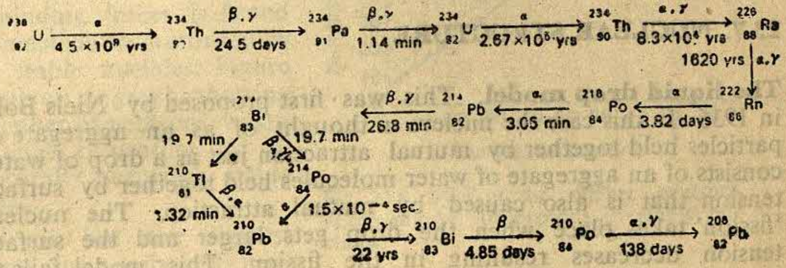


Fig. 23.5. Uranlum series.

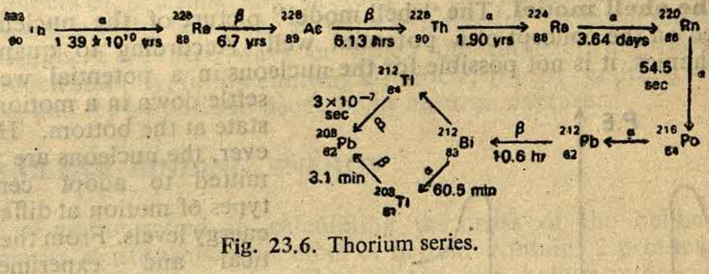


Fig. 23.6. Thorium series.

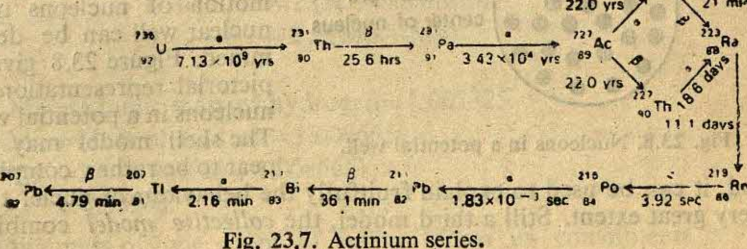


Fig. 23.7. Actinium series.

The first series is uranium series. It begins with $^{239}_{92}U$ and decays to $^{206}_{82}Pb$. This series is also known as $4n+2$ series. The second series is $^{232}_{90}Th$ nuclide and its radioactive descendants. This is known as thorium series. The mass number of each member of the series is exactly divisible by four and the series is also sometimes referred to as $4n$ series. The third series, known as the actinium series, actually has $^{235}_{92}U$ as the parent nuclide and the last member of the series is $^{207}_{82}Pb$. This is also known as $4n+3$ series. The members of each of the respective radioactive series are all in secular equilibrium with the very long-lived parent nuclide.

23.7. NUCLEAR STRUCTURE

The liquid drop model. This was first proposed by Niels Bohr in 1936. In this case the nucleus in thought of as an aggregate of particles held together by mutual attraction just as a drop of water consists of an aggregate of water molecules held together by surface tension that is also caused by mutual attraction. The nuclear 'fission' takes place when the drop gets larger and the surface tension decreases resulting in the fission. This model fails to account for the origin of force that holds the particle in this "drop" form.

The shell model. The "shell model" picture of the nucleus is based on the concept of a potential well. According to quantum mechanics, it is not possible for the nucleons in a potential well to settle down in a motionless state at the bottom. However, the nucleons are permitted to adopt certain types of motion at different energy levels. From theoretical and experimental studies of nuclei, the order of the different states of motion of nucleons in a nuclear well can be determined. Figure 23.8 gives a pictorial representation of nucleons in a potential well. The shell model may appear to be rather complicated, it can be used to explain fruitfully the behaviour of nuclei to a very great extent. Still a third model, the *collective model* combines

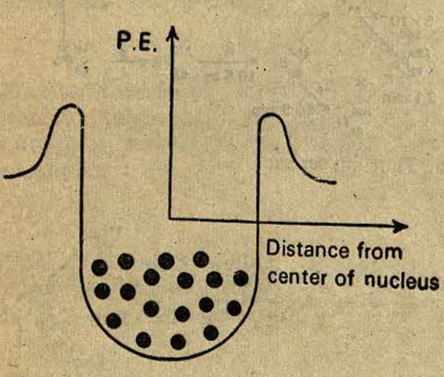


Fig. 23.8. Nucleons in a potential well.

the more successful features of the shell model with those of the liquid drop model.

23.8. STABILITY OF THE NUCLEI

Rutherford's experiments in which the metal foils were bombarded with alpha particles demonstrated that the radius of an atomic nucleus is about 10^{-13} cm. When several protons are brought together to within a distance corresponding to the nuclear radius, very strong binding forces are required to overcome the repulsive forces between the positively charged particles. An answer to the nature of these binding forces is found in the neutron-to-protonr atios of the stable nuclides. Figure 23.9 gives a graph showing the number of neutrons versus the number of protons for all the naturally occurring stable nuclides.

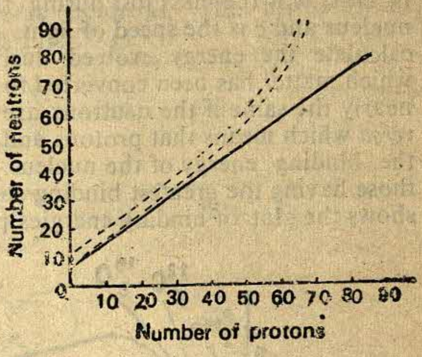


Fig. 23.9. Plot of the number neutrons *vs* the number of protons in stable nuclides.

For all but the lightest elements, the number of neutrons, exceed the number of protons The stable nuclides lie within a "belt of stability" which rises above the line drawn to represent equal numbers of neutrons, and protons. If the neutron-to-proton ratio of a nucleus lies below the stability belt for the given number of protons, there are three ways in which the radioactive species can approach stability, (*a*) by emitting α-particle, (*b*) by emitting a β-particle, and (*c*) by position decay or by electron capture.

23.9. NUCLEAR BINDING ENERGY

Suppose we are interested in calculating the mass of the helium atom from its constituents. One atom of helium contains 2 protons, 2 neutrons and 2 electrons. In other words, one helium atom is equivalent to 2 hydrogen atoms and 2 neutrons, so that,

$$1 \text{ He atom} = 2\,(\text{H} + 1 \text{ neutron})$$
$$= 2 \times (M_H + M_N)$$

where,

M_H = Atomic mass of hydrogen = 1.007825

M_N = Mass of neutron = 1.008665

$$M_{He} = 2 \times (1.007825 + 1.008665)$$
$$= 4.03298.$$

Thus the mass of one atom of helium from its constituents is

4.03298. Form the table, the measured mass of helium atom $^{4}_{2}$He is 4.002603. This is 0.03 less than the estimated value. It would appear that the actual mass of a nuclide is never equal to the sum of the masses of its constituents. This is known as mass defect and the energy equivalent to this missing mass is known as the binding energy of the nucleous. Binding energies of nuclei may be calculated using Einstein's equation, $E=mc^2$, where E is the energy in ergs, m is the mass lost during the fusion of particles to form nucleus and c is the speed of light. This equation can be used to calculate the energy evolved during any radioactive process in which matter has been converted to energy. Nuclear forces are very nearly the same if the neutrons are replaced by protons and *vice versa* which means that protons and neutrons contribute equally to the binding energy of the nucleus. The most stable nuclides are those having the greatest binding energy per nucleon. Figure 23.10 shows the plot of binding energies per nucleon *vs* mass number.

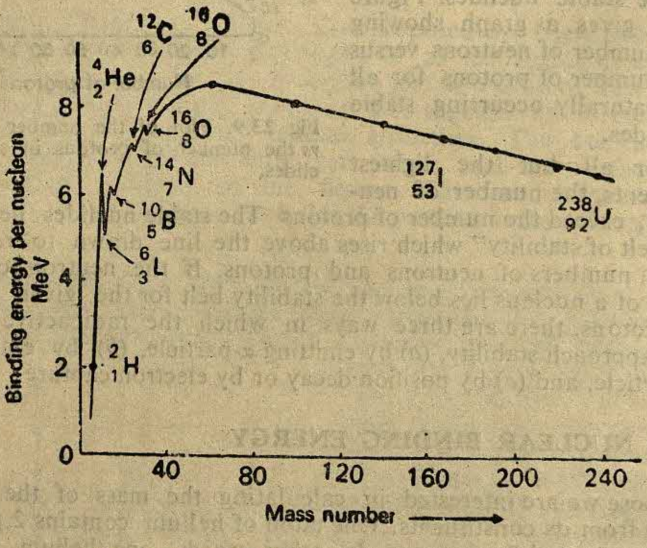


Fig. 23.10. Plot of binding energy *vs* mass number.

Problem 23.3. Calculate the binding energy and the binding energy per nucleon in an atom of fluorine-19, mass=18.99840 amu.

Solution. A fluorine-19 nucleus will have 9 protons and 10 neutrons. The mass of 9 protons and 10 neutrons is

$$9\times1.007276+10\times1.008665=19.152134 \text{ amu}.$$

One mole of fluorine atoms weighs 18.99840 g.

$$\text{Weight lost/mole}=19.152134 \text{ g/mole} - 18.99840 \text{ g/mole}$$
$$=0.153734 \text{ g/mole}.$$

$$\therefore \text{ Weight lost/atom} = 0.153734 \text{ g/mole} \times \frac{1 \text{ mole}}{6.02\times10^{23} \text{ atoms}}$$

23.10. NUCLEAR FISSION

The absorption of a neutron by most isotopes involves radiative capture, with excitation energy appearing as a gamma ray. In certain heavy elements, notably uranium and plutonium an alternate consequence is observed—the splitting of nucleus into two massive fragments. The process is called nuclear fission, and was observed by O. Hahn and F. Strassman. They observed that ${}^{235}_{92}U$ can be induced to fission by low energy neutrons. The fission process sequence of events are shown in Fig. 23.11.

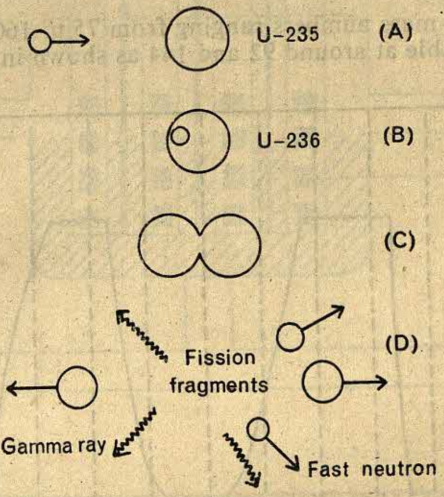


Fig. 23.11

In stage A, the neutron approaches the U—235 nucleus and it is absorbed. The product U-236 formed in stage B is in the excited state. The excess energy in some interactions may be released as a gamma ray, but more frequently, the energy causes distortions of the nuclens into a dumbbell shape as shown in stage C. The parts of the nucleus oscillate in a manner analogous to the motion of a drop of liquid. Due to the high electrostatic repulsion over nuclear attraction, the two parts may get separated as shown in stage D. These are called fission fragments.

The initial nucleus is nearly spherical but in order to form two fragments of comparable size it must become deformed, in elongated form, the nucleus has increased potential energy, but as the deformation continues, the repulsion between the electric charges in the fragment decreases. The potential energy of the system again drops and finally results in fission. In this process energy of the order of 200 MeV is released. The substances that give rise to fission with slow neutrons are called fissile.

In the fission process large number of neutrons are released which are all important for practical application to a self-sustaining chain reaction. The number that appears depends on the isotope and the bombarding neutron energy. For example, in U-235 with slow neutrons the average number is 2.43. The nuclear reaction equation for fission resulting from neutron absorption in U-235 may be symbolised as under

$$ {}^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{A_1}_{Z_1}\mathrm{F}_1 + {}^{A_2}_{Z_2}\mathrm{F}_2 + \nu\, {}^{1}_{0}\mathrm{n} + \text{energy} $$

where F_1 and F_2 are chemical symbols for the two fragments obtained in splitting.

Generally the mass numbers ranging from 75 to 160 are observed with most probable at around 92 and 144 as shown in Fig. 23.12.

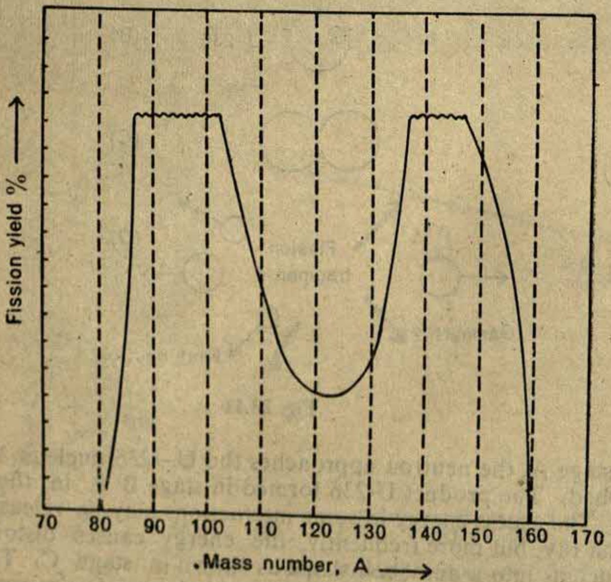


Fig. 23.12. Yield of fission products by mass number.

The speed of neutrons is reduced with the help of suitable modetors. The moderators which are commonly used are graphite, paraffin and heavy water (D_2O). For any given fissionable system, there is thus a minimum critical size below which the maintenance of a fission chain is impossible.

23.11. NUCLEAR REACTOR

In atomic bomb two pieces of pure U-235 or Pu-239 each below the critical size are brought together to form one piece larger than the critical size. Fission of U-235 or Pu-239 proceeds in an in controlled manner as an exploding chain reaction. Fig. 23.13 shows the diagram of the commonest type of nuclear reactor.

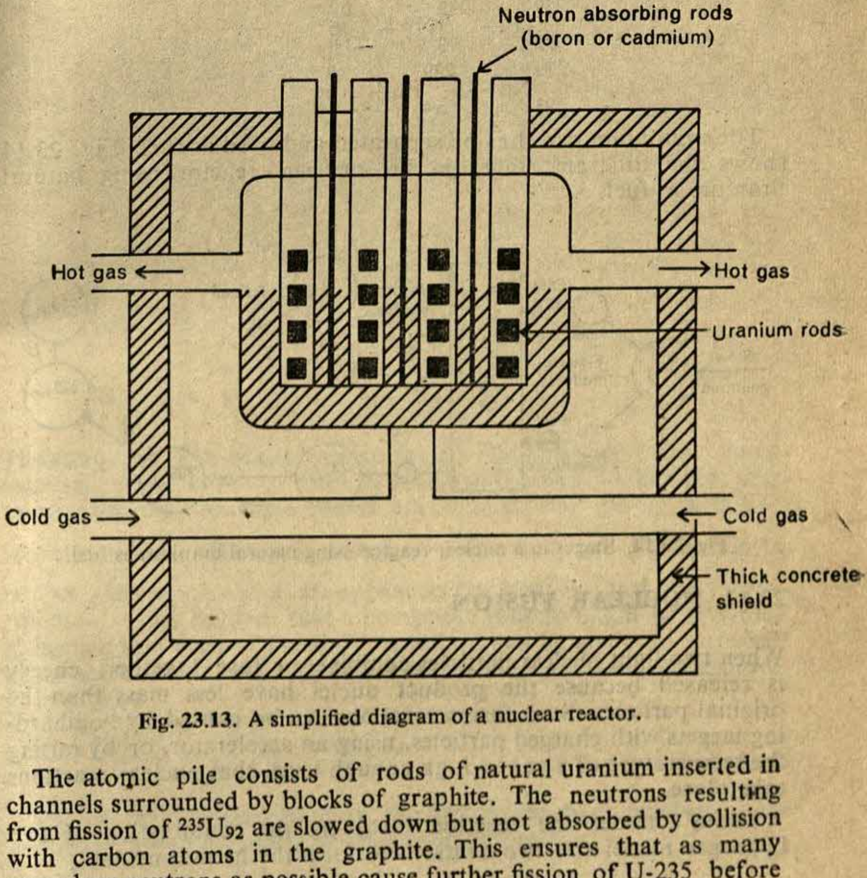


Fig. 23.13. A simplified diagram of a nuclear reactor.

The atomic pile consists of rods of natural uranium inserted in channels surrounded by blocks of graphite. The neutrons resulting from fission of $^{235}U_{92}$ are slowed down but not absorbed by collision with carbon atoms in the graphite. This ensures that as many secondary neutrons as possible cause further fission of U-235 before escaping from the pile or before capture by the more plentiful U-238 atoms. The temperature of the pile can be controlled by movable rods of boron or cadmium which absorb neutrons. The deeper these rods are inserted, the more neutrons are absorbed and the fewer fissions take place. By carefully adjusting the positions of these rods a controlled chain reaction can be obtained with a steady and continuous production of energy. The heat produced during the fission process is removed by a stream of circulating carbon dioxide. The hot gas can be used to make steam and then drive a turbine.

Besides liberating energy, the atomic reactor also produces plutonium as a result of the neutron bombardment of U-238, according to the following reactions.

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{92}\mathrm{U}$$

$$^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\mathrm{e}$$

$$^{239}_{93}\mathrm{Np} \rightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\mathrm{e}$$

The plutonium can thus be separated and used as fuel. Fig. 23.14 shows the different stages in a nuclear reactor using natural uranium as fuel.

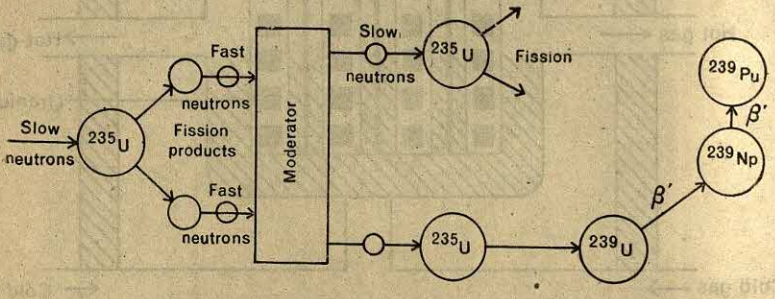


Fig. 23.14. Stages in a nuclear reactor using natural uranium as fuel.

23.12. NUCLEAR FUSION

When two light nuclear particles combine or fuse together, energy is released because the product nuclei have less mass than the original particles. Such fusion reactions can be caused by bombarding targets with charged particles, using an accelerator, or by raising the temperature of a gas to high enough level, that nuclear reactions take place.

Let us consider the reaction involving the combination of two hydrogen nuclei and two neutrons to form the helium nucleus,

$$2\,{}^{1}_{1}\mathrm{H} + 2\,{}^{1}_{0}\mathrm{n} \rightarrow {}^{4}_{2}\mathrm{He}$$

The mass difference using atomic masses is

$$2\,(1.007825) + 2\,(1.008665) - 4.002603 = 0.030377 \text{ amu},$$
$$= 28.2 \text{ MeV}$$

A comparable amount of energy would be obtained by combining four hydrogen nuclei to form helinm plus two positrons.

$$4\,{}^{1}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{1}\mathrm{e}$$

This reaction takes place in the sun and other stars through the so called carbon cycle in a complicated chain of events involving hydrogen and isotopes of the elements carbon, oxygen and nitrogen. The sun's large yield of energy is due to its tremendous mass of materials.

In the "hydrogen bomb", on the other hand, the high temperatures created by a fission reaction cause the fusion to proceed in a rapid and uncontrolled manner. The most promising-fusion reactions make use of isotope deuterium. Four reactions are important in the process of fusion.

$$^{2}_{1}\text{H} + {}^{2}_{1}\text{H} \rightarrow {}^{3}_{1}\text{H} + {}^{1}_{1}\text{H} + 4.03\ \text{MeV}$$

$$^{2}_{1}\text{H} + {}^{2}_{1}\text{H} \rightarrow {}^{3}_{2}\text{He} + {}^{1}_{0}\text{n} + 3.27\ \text{MeV}$$

$$^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \rightarrow {}^{4}_{2}\text{He} + {}^{1}_{0}\text{n} + 3.27\ \text{MeV}$$

$$^{2}_{1}\text{H} + {}^{3}_{2}\text{H} \rightarrow {}^{4}_{2}\text{He} + {}^{1}_{1}\text{H} + 18.3\ \text{MeV}$$

The fusion of two deuterons-deuterium nuclei is known as D-D reaction. This results in two processes of equal likelihood. The other reactions yield more energy but involve the use of artificial isotopes tritium $^{3}_{1}$H, and helium-3. We also find that the products of first and second equations appear as reactants in third and fourth equations. This suggests that a composite process might be feasible. Assuming that each of the above reactions can be made to proceed at the same rate, along with twice the reaction of neutron capture in hydrogen.

$$^{1}_{1}\text{H} + {}^{1}_{0}\text{n} \rightarrow {}^{2}_{1}\text{H} = 2.2\ \text{MeV}$$

On adding all these equations, we get the reaction involving the conversion of deuterium into helium according to

$$4\ {}^{2}_{1}\text{H} \rightarrow 2\ {}^{4}_{2}\text{He} + 47.7\ \text{MeV}$$

The energy yield per atomic mass unit of deuterium fuel would thus be about 6 MeV, which is much more favourable than the yield per atomic mass unit of U-235 burned which is only

$$\frac{190}{235} = 0.85\ \text{MeV}.$$

A fusion reactor provides power from a controlled fusion reaction.

23.13. NUCLEAR REACTIONS

Nuclear reactions are processes in which some change in the character of the nucleus takes place, either spontaneously or as the result of bombardment by a particle or ray.

The conservation of mass-energy is a firm requirement for any valid nuclear reaction. A systematic description of nuclear reactions has been developed to account for experimental observations. Suppose that a particle labled *a* striks a nucleus *X* to produce a compound nucleus *C*, where the asterisk implies that the nucleus contains extra internal energy of motion of the nucleons, called excitation energy.

The compound nucleus then disintegrates to release the particle *b* and *a* residual nucleus Y. These reactions may be symbolised as under

$$a+X \rightarrow C$$

$$C \rightarrow Y+b$$

The net effect being

$$a+X \rightarrow Y+b$$

This reaction can be abbreviated as *X* (*a*, *b*) *Y*, which implies that particle *a* comes in and particle *b* goes out. The symbols *a* and *b* may stand for the neutron (*n*), alpha particle (α), deutron (*d*), gamma ray (γ), proton (*p*), triton (*t*), the nucleus or tritium and so on.

There are many similarities between the two types of reactions, even though they occur in quite different energy regions and with different mechanisms.

Individual particles are involved in each case, nucleons in nuclei and atoms in molecules respectively. Laws of conservation of energy apply to each—that of charge, number of particles involved and mass-energy. Let us write down a chemical reaction describing the formation of water

$$2H+O=H_2O$$

The number of atoms of hydrogen and oxygen are the same on both sides, there is a valence balance, with +1 for hydrogen and −2 for oxygen; 2.4 eV energy is released in the process. Let us now compare this with the reaction of a neutron with a proton as the nucleus of hydrogen, to form a deuteron, as the nucleus of deuterium.

$${}_0^1n+{}_1^1H \rightarrow {}_1^2H+\gamma$$

The total number of nucleons is the same on both sides; the total nuclear charge is balanced; energy is released here in the form of gamma ray, of about 2.2 MeV. Thus we see that the energy release in this nuclear reaction is about a million times as great as for the chemical reaction.

TABLE 23.1
Examples of Nuclear Reactions

Type	*Reaction*	*Radioactivity of Product-Nuclide*
(α, η)	${}^{75}_{33}\mathrm{As} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{78}_{35}\mathrm{Br} + {}^{1}_{0}\eta$	β^+
(α, p)	${}^{106}_{46}\mathrm{Pd} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{109}_{47}\mathrm{Ag} + {}^{1}_{1}\mathrm{H}$	stable
(p, η)	${}^{7}_{3}\mathrm{Li} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{7}_{4}\mathrm{Be} + {}^{1}_{0}\eta$	ec
(p, γ)	${}^{14}_{7}\mathrm{N} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{15}_{8}\mathrm{O} + \gamma$	β^+
(p, α)	${}^{9}_{4}\mathrm{Be} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{6}_{3}\mathrm{Li} + {}^{4}_{2}\mathrm{He}$	stable
(d, p)	${}^{31}_{15}\mathrm{P} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{32}_{15}\mathrm{P} + {}^{1}_{1}\mathrm{H}$	β^-
(d, n)	${}^{209}_{83}\mathrm{Bi} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{210}_{84}\mathrm{P}_0 + {}^{1}_{0}\eta$	α
(n, γ)	${}^{50}_{27}\mathrm{Co} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{60}_{27}\mathrm{Co} + \gamma$	β^-
(n, p)	${}^{45}_{21}\mathrm{Sc} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{45}_{20}\mathrm{Ca} + {}^{1}_{1}\mathrm{H}$	β^-
(n, α)	${}^{27}_{13}\mathrm{Al} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{24}_{11}\mathrm{Na} + {}^{4}_{2}\mathrm{He}$	β^-

The elements following uranium in the periodic table are called the transuranium elements. These elements do not occur in nature but many have been produced by nuclear reactions. Some of these reactions use targets of artificial nuclides, and in these cases the final products are therefore the result of synthesis consisting of several steps. Some of the common examples are:

$${}^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{92}\mathrm{U} + \gamma$$

$${}^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\mathrm{e}$$

$${}^{239}_{93}\mathrm{Np} \rightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\mathrm{e}$$

$${}^{239}_{94}\mathrm{Pu} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{240}_{95}\mathrm{Am} + {}^{1}_{0}\mathrm{n}$$

$${}^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{242}_{96}\mathrm{Cm} + {}^{1}_{0}\mathrm{n}$$

$${}^{238}_{92}\mathrm{U} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{244}_{98}\mathrm{Cf} + 6{}^{1}_{0}\mathrm{n}$$

$${}^{238}_{92}\mathrm{U} + {}^{14}_{7}\mathrm{N} \rightarrow {}^{246}_{99}\mathrm{Es} + 6\,{}^{1}_{0}\mathrm{n}$$

$${}^{238}_{92}\mathrm{U} + {}^{16}_{8}\mathrm{O} \rightarrow {}^{250}_{100}\mathrm{Fm} + 4{}^{1}_{0}\mathrm{n}$$

$${}^{252}_{98}\mathrm{Cf} + {}^{10}_{5}\mathrm{B} \rightarrow {}^{257}_{103}\mathrm{Lw} + 5\,{}^{1}_{0}\mathrm{n}$$

Nuclear reactions differ from ordinary chemical reactions in the following respects:

(*a*) Nuclear reactions involve change in atomic numbers.

(*b*) The sum of the mass numbers is unchanged, the total quantity of matter is changed appreciably.

(*c*) The quantities are defined per particle rather than per mole.

(*d*) Nuclear reactions are those of the specific nuclides rather than of the mixture of isotopes comprising the element.

23.14. MASS SPECTROMETRY

The atomic weights of elements, detection of the elements and their molecular mass can be determined using mass spectrometry.

There are various types of mass spectrometers. The first mass spectrometer dates back to the work of J.J. Thomson and F.W. Aston. The mass spectrometer produces charged ions consisting of the parent ion and the ionic fragments of the original molecule and sorts these ions according to their mass/charge ratio. The mass spectrum is a record of the number of different kinds of ions—the relative numbers of each are characteristic for every compound, including isomers. The substance to be studied in a mass spectrometer should be able to exist in the gaseous state at the temperature and pressure existing in the ion source. The essential components of a mass spectrometer are shown in Fig. 23.15.

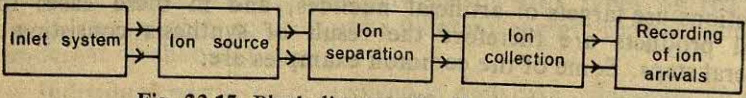


Fig. 23.15. Block diagram of a Mass spectrometer.

A brief discussion of these components are as follows: (*a*) Inlet systems; (*b*) Ion sources; (*c*) Separation of Ions; (*d*) Recording of spectra.

Inlet Systems

There are several means of introducing the sample into mass spectrometer and the inlet system used will normally depend on the volatility of the sample.

(*i*) **Cold inlet**. Gases or compounds which are very volatile at room temperature and a pressure of 10^{-2} torr are allowed to 'leak' into the mass spectrometers through a glass sinter and led along a glass tube into the ion source. The pressure inside the mass spectrometer is about 10^{-6} torr.

(*ii*) **Hot inlet**. This is similar to the cold inlet except that it may be heated to about 300°C to volatilise organic compounds which are then led along a heated line to the ion source.

(*iii*) **Direct inlet.** The compounds which are not sufficiently volatile to be introduced through the hot or cold inlets may be inserted directly into the ion source by means of a probe passing through a vacuum lock. At low pressure of the order of 10^{-6} torr and increasing the temperature most of the compounds are sufficiently volatile to yield a mass spectra.

Ion Source

An ion source may be defined as the region in which ionisation occurs. This is enclosed in a chamber in which the sample is ionised. The ions produced are pushed out towards the exit slit by a low positive potential inside the chamber and then accelerated through a high potential of 2-8 kV and passed away into the mass spectrometer for separation according to mass/charge ratio. The common means of ionising organic compounds are ***photons***. The ionization potentials of most organic compounds lie below 13 electronvolts so that high intensity short wavelength radiation can be used for ionization. The helium discharge at 21.21 eV provides a convenient source of photons able to ionise all organic compounds.

Electrons. Electrons, obtained from a heated filament in vacuum are accelerated through some voltage and directed across the ion chamber. The voltage is continuously variable between 5-100 volts and by convention standard mass spectra are obtained at 70 volts because maximum ion yield is obtained at this value.

Electric fields. By applying a high positive electric potential on an electrode in the shape of a point, sharp edge or fine wire, a very high potential gradient is produced in the regions of high curvature. The positive ion so formed is immediately repelled by the positive electrode into the mass spectrometer. This method poses some difficulties in focussing the ions into a beam, because the initially produeed ions are repelled by the high positive potential on the electrode immediately after formation.

Chemical ionisation. The collision of an ion and a molecule can lead to reaction giving a new charged species. Thus the ion-molecule reaction between methane ion and a methane molecule gives rise to the unusual and fairly stable CH^+_5 species according to the reaction,

$$CH_4^+ + CH_4 \rightarrow CH^+_5 + CH_3.$$

For effective ion-molecule reaction it is necessary to operate at source pressures of about 10^{-4} torr.

Combined sources. It is often an advantage to be able to generate mass spectra of organic materials by two different ionization methods. It is for this reason that combined electron-impact/field ionisation and electron-impact/chemical-ionization sources have been constructed in either of the two possible modes.

Separation of Ions

The separation of ions to their mass to charge ratio can be achieved with magnetic and electric fields alone or combined. The basic differences between the various types of mass spectrometers lie in the manner in which such fields are used to effect separation.

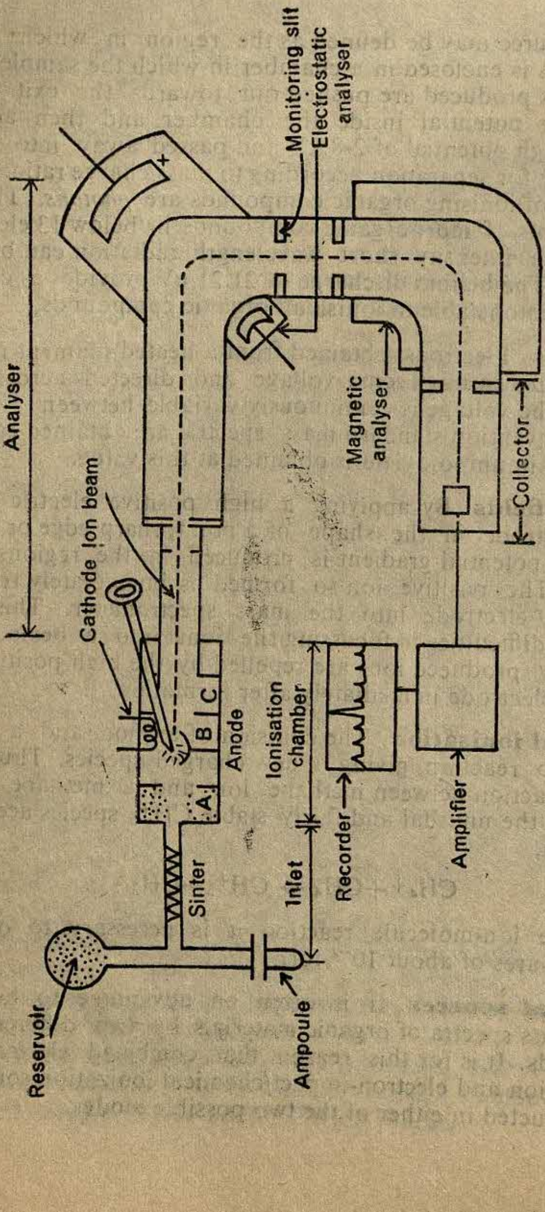


Fig. 23.16.

After the beam of ions has been accelerated through a potential of 6000-8000 volts away from the ion source, it is divergent and slits are used to reduce the spread. The ion beam then passes between a pair of smoothed curved metal plates called an electro-static analyser because the electric potential maintained across the plates focusses the ion beam at a second slit. The electrostatic analyser is an energy focussing device. The equations of motion governing the motion of the ions through an analyser are the following:

Kinetic energy of the ions, $\frac{1}{2}mv^2 = eV$ . . . (23.5)

where e is charge on the ion that are accelerated initially by applying a potential V, m is the mass of the ion and v is the velocity. Since the ions are deflected in a curvature of radius r in a field in electric sector, B. At equilibrium,

$$\frac{mv^2}{r} = eBv \qquad \ldots (23.6)$$

On combining the two equations (23.5) and (23.6) we get,

$$\frac{2eV}{m} = \frac{eBr^2}{m}$$

$$\frac{m}{e} = \frac{B^2r^2}{2V} \qquad \ldots (23.7)$$

Thus ions accelerated through a potential (V) and passing through a uniform field (β) have the same radius of curvature (r). Thus, if the field B is kept constant, the electric sector focusses the ions according to their translational energies.

The energy-focussed ion beam is then passed through a magnetic field where the mass separation is effected. After acceleration from the ion source, the ions possess a translational energy $\frac{1}{2}mv^2$. On passing through the magnetic field, the ions experience on centrifugal force due to the constraint (HeV) imparted by the magnetic field (H). We can write the following relationship,

$$eV = \frac{1}{2}mv^2 \qquad \ldots (23.8)$$

$$Hev = \frac{mv^2}{r} \qquad \ldots (23.9)$$

$$\frac{m}{e} = \frac{H^2.r^2}{2.V} \qquad \ldots (23.10)$$

At constant values of the magnetic field (H) and the accelerating potential (V), each values of m/e will correspond to a radius of curvature r. Thus after separation in the magnetic field singly charged ions of mass m_1, m_2, m_3 will be brought to foci f_2, f_2, f_3, corresponding to radii of curvature r_1, r_2, r_3. If an electric detector is placed at f_1 then arrival of ions (m_1/e) will be recorded and if other detectors were placed at f_2, f_3 the ions (m_2/e), (m_3/e). (m_3/e), would also be recorded. Instead of having detectors at f_1, f_2 and f_3, it is convenient to vary the magnetic field (H) continuously so that each m/e species is brought to focus at f_1 *i.e.* the radius of curvature (r) is kept constant. This is called the magnetic scanning of the spectrum. It is also possible to vary the electrical accelerating voltage (V), with H constant to bring each m/e species to the same focus. This method is called electrical scanning and is less frequently applied because the sensibility of the instrument decreases on increasing the voltage. The combined use of electric and magnetic analyser gives double focussing mass spectrometer because the ion beam is focussed first for translational energy and then for mass to charge ratio. This is shown in the Fig. 23.16.

Recording of Spectra

The electrical signals from the detector are amplified and passed to a recording device. A pen recorder may be used but this means the spectrum must be scanned rather slowly because of the relatively slow response time of the pen mechanism. Alternatively the amplified signals are used to deflect mirror galvanometers and ultraviolet light reflected from them is focussed into sensitized paper to give a permanent record. The photographic plate method of detection of ions provides its own record of the spectrum and the electrical signals from the microdensitometers can of the plate is fed to the computer to generate the mass spectrum.

The choice of design for the mass spectrometer depends on the requirement of (*i*) the range of masses which must be covered (*ii*) the resolution and (*iii*) the sensitivity. The term resolution is defined as the ratio $M/\triangle M$, where $\triangle M$ is the difference in mass numbers which will give a valley of 10 per cent between peaks of mass numbers M and $M+\triangle M$ where the two peaks are of equal heights. Resolution is considered satisfactory if $\triangle M > 1$. The resolution is generally not uniform over the whole range of makes can be

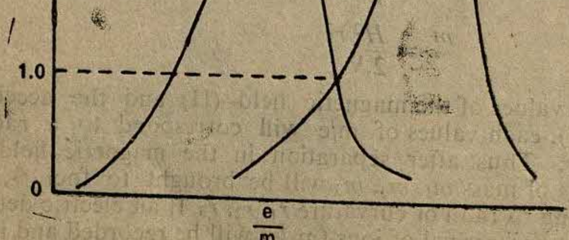


Fig. 23.17. Resolution of a Mass spectra.

detected, it becomes proper at higher mass numbers. This is shown in the mass spectrum of different isotopes of lead is shown in Fig. 23.18.

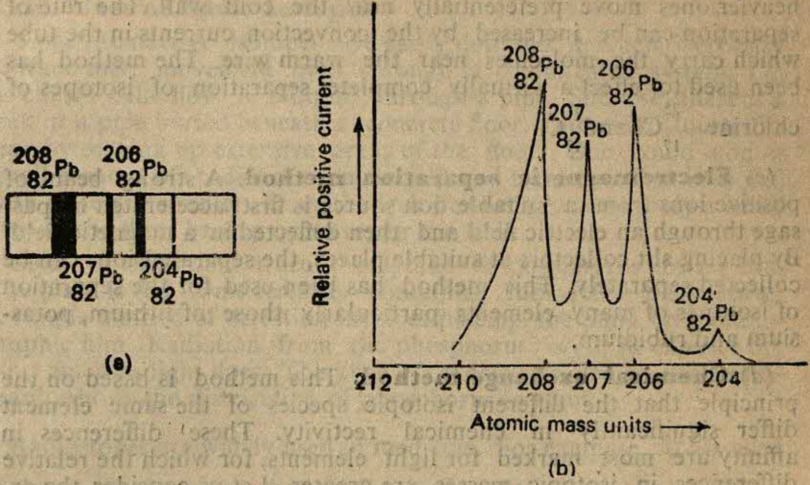


Fig. 23.18. A mass spectrum of lead (*a*) on a film; (*b*) detected electrically. The intensities of the lines are proportional to the number of ions of the particular isotope of lead.

23.15. THE SEPARATION OF ISOTOPES

The separation of isotopes is a very tedious process and there are numerous methods employed for their separation. Some of the important methods are the following:

(*a*) Gaseous diffusion method
(*b*) Thermal diffusion method
(*c*) Electromagnetic separation method
(*d*) Chemical exchange method.

(*a*) **Gaseous diffusion method.** The method makes use of the different rates of diffusion of gaseous isotopic nuclides. Since the rate of diffusion of a gas is inversely proportional to the square root of its density, a separation can be carried out by using a number of diffusion units in series. The method has been used to separate $^{235}UF_6$ from $^{238}UF_6$. However, by the use of several thousand diffusion stages, which operates like a fractionating column in distillation, the 90 atomic per cent of $^{238}_{92}U$ has been separated.

(*b*) **Thermal diffusion method.** This method has been successfully employed by Clausius in 1938. It involves a combination of diffusion and convection. The experimental arrangement consists of a long vertical cylindrical pipe and is heated electrically to a temperature of 500°C. A temperature gradient is maintained between the hot wire and the cold outer walls, with the result that the lighter isotope molecules tend to collect near the hot wire, whereas the heavier ones move preferentially near the cold wall. The rate of separation can be increased by the convection currents in the tube which carry the molecules near the warm wire. The method has been used to effect a virtually complete separation of isotopes of chlorine $^{35}_{17}Cl$ and $^{37}_{17}Cl$.

(*c*) **Electromagnetic separation method**. A strong beam of positive ions from a suitable ion source is first accelerated by passage through an electric field and then deflected in a magnetic field. By placing slit collectors at suitable places, the separated ions can be collected separately. This method has been used for the separation of isotopes of many elements particularly those of lithium, potassium and rubidium.

(*d*) **Chemical exchange method.** This method is based on the principle that the different isotopic species of the same element differ significantly in chemical rectivity. These differences in affinity are most marked for light elements, for which the relative differences in isotopic masses are greater. Let us consider the exchange of isotopes of nitrogen of mass numbers ^{14}N and ^{15}N respectively, between ammonia gas and ammonium ion present as an ammonium salt in solution. The reaction can be represented as follows:

$$N^{15}H_3(gas) = N^{14}H^{+}_4(aq) = N^{14}\,H_3(gas) + N^{15}\,H^{+}_4(soln)$$

After the equilibrium was attained in the exchange columns, ^{15}N could be removed as nitrate. Urey has applied the chemical exchange method for the determination of the temperature of seas in remote geologic within 1°C from the ^{18}O : ^{16}O ratio in deposists of the shells of prehistoric molluses.

TABLE 23.3

Physical properties of H_2O and D_2O

Property	*Ordinary water* *H_2O*	*Heavy water* *D_2O*
Density at 25°C	1.0000 gm/c.c.	1.1079 gm./c.c.
Maximum density at	4°	11.6°
Freezing point	0.00°C	3.82°
Boiling point	100.00°	101.42°
Surface tension (20°C)	72.75 dynes cm^{-1}	67.8 dynes cm^{-1}
Viscosity (10°C)	13.10 millipoise	16.85 millipoise

Heavy hydrogen. On careful examination of the spectrum of hydrogen, H.C. Urey in 1931 established the existence of the hydrogen isotope with mass 2. This was called heavy hydrogen or deuterium. The water in which heavy hydrogen is present is called heavy water (D_2O). Some of the properties of hevy water and ordinary water are listed in Table 23.3.

23.16. Uses of Radio Isotopes

Since radioactive isotopes are easily detected, it is relatively easy to trace their movement even through a complicated system. Let us consider the flow of a liquid through a pipe. Suppose there is a leak in a pipe buried beneath a concrete floor. One could locate the leak by digging up extensive areas of the floor. One could add a small amount of radioactive material, and trace the flow of liquid with a Geiger counter. Once the leak has been located, only a small area of the floor be dug up to repair the leak.

Similarly one could trace the uptake of phosphorus by a plant. The plant is fed some fertiliser containing radioactive phosphorus. A simple method of detection involves placing the plant on a photographic film. Radiation from the phosphorus isotopes exposes the film, much as light does. This type of exposure called an autoradiograph, shows the districution of phosphorus in plant.

Radiostopes are widely used in medicine. For example $^{131}_{83}I$ is used to determine the size, shape and activity of the thyroid gland. The body concentrates iodine in this gland. Radioactive iodine behaves exactly in the same manner in the body, but it can be detected from outside the body. In order to know the size and location of thyroid tumor, diagonistician will prescribe iodine cocktail. Table 23.4 gives briefly the use of radio isotopes in medincine.

Radioisotopes have also been used extensively

TABLE 23.4

Some radioisotopes and their application in medicine

Isotope	*Name*	*Use (s)*
^{74}As	Arsenic—74	Locate brain tumors
^{51}Cr	Chromium—51	Determine the volume of red blood cells. Determine the total blood volume.
^{58}Co	Cobalt—58	Determine uptake of vitamin B_{12}
^{60}Co	Cobalt—60	Radiation treatment of cancer
^{59}Fe	Iron—59	Measure rate of formation and life time of red blood cells.
^{131}I	Iodine—131	Detection of thyroid malfunction and measure liver activity.
^{32}P	Phosphorus—32	Detected skin cancer or cancer exposed by surgery.
^{226}Ra	Radium—226	Radiation therapy for cancer
^{24}Na	Sodium—24	Detect constrictions and obstructions in the circulatory system.
^{3}H	Trititum	Determine total body water.

The structure of DNA within the genes of animals and plants can be changed by radiation. For reasons not yet clear, cancer cells are more susceptible than normal cells to destruction by radiation. Thus γ-rays can be used for the treatment of cancer. Penetrating γ-rays from cobalt-60 is used in treating inaccessible growths. where as superficial cancers such as skin cancer can be treated by less penetrating radiation from $^{32}_{15}P$ or $^{90}_{38}Sr$ in plastic sheets strapped an the affected area.

The radiation passing through a material decreases as the material gets thicker. Thus the amount of penetrating beta or gamma radiation can be used to estimate the thickness of various materials such as paper or plastic. The advantage using radiation for measuring the thickness is that there need be no touching, marking or tearing of the article concerned. The radiation thickness gauges can be used to control thickness up to 0.2 cm steel.

A similar use of radioactive isotopes is made in level gauges and empty packet detectors. The level of liquid in a closed vessel can be found by placing a source on one side of the container and detector on the other. These are then moved down, a sudden decrease in the detected radiation shows the level of the liquid. Level gauges of this type are used to measure the level of liquids in fire extinguishers and gas cylinders. Similarly empty-packet detectors can be used to reject empty or insufficiently filled packets of biscuits or cigarettes.

23.17. HAZARDS OF NUCLEAR RADIATIONS

We have seen radioisotopes are used in beneficial ways. But radiations also present a hazard to living things. High energy particles and rays knock electrons from atoms, forming ions. Such chemical changes when they occur in living cells, can be highly disruptive. This can decrease the white blood cells in the body. Radiation also effects bone narrow, causing a drop in the production of real blood cells and resulting in anemia. Radiation also has been shown to induce leukemia, a cancer like disease of blood forming organs. Radiation also causes changes in the molecules of heredity, in reproductive cells. Such changes show up as mutations in the offsprings of exposed parents. However, most of the mutations during the evolution of present species may have been caused by radiation from ever present cosmic rays and from natural radio activity in air, water, soil and rocks.

Animals and plants tend to concentrate some radioactive isotopes. For example, ^{131}I is a product of nuclear fission. It is readily taken up by plants. Cows eat the plants and further concentrate in their milk. Humans drink the milk and further concentrate the ^{131}I, particularly in thyroid glands which can cause radiation damage. Concern over radiation damage from nuclear fallout led to a movement to ban the atmospheric testing of nuclear weapons.

PROBLEMS

1. How many types of radioactive radiations are known and how are they distinguished?

2. (*a*) Define half-life period of a radioactive substance.

(*b*) A sample of uranite, a uranium containing mineral, was found on analysis to contain 0.214g of lead for every gram of uranium. Assuming that all the lead resulted from the radioactive disintegration of the uranium since the geological formation of the uranite, and that all isotopes of uranium other than U^{238} can be neglected, estimate using the dalta, when the mineral was formed in the earth's crust. The half life of ^{238}U is 4.5×10^9 years.

Ans. 1.4×10^9 years.

3. Explain the term 'radioactive decay constant.' How is it related to the half-life-period of a radioactive substance. The half-life of ^{226}Ra is 1620 years. (*a*) Calculate its decay constant in units of sec^{-1}. (*b*) Calculate the number of disinte rations of 1 gm of Ra^{223}.

Ans. 1.36×10^{-11} sec^{-1}; 3.6×10^{10} dis/sec.

4. Determine the number of:

(*a*) Nuclear protons, (*b*) nuclear nutrons, (*c*) electrons, in each of the following atoms:

(*i*) Ge^{70}, (*ii*) Ge^{72}, (*iii*) Be^9, (*iv*) U^{235}.

Ans. (*i*) (*a*) 32 ; (*b*) 38 ; (*c*) 32,
(*ii*) (*a*) 32 ; (*b*) 40 ; (*c*) 32,
(*iii*) (*a*) 4 ; (*b*) 5 ; (*c*) 4,
(*iv*) (*a*) 92 ; (*b*) 143; (*c*) 92.

5. State and explain the group displacement law in radioactivity. How does it lead to the idea of radioactive isotopes?

6. (*a*) Give a brief account of artificial radioactivity.

(*b*) Complete the following equations:

(*i*) $_{11}Na^{23} + _2He^4 \rightarrow _{12}Mg^{26} + ?$
(*ii*) $_{29}Cu^{64} \longrightarrow 1\beta^{\circ} + ?$
(*iii*) $Ag^{190} \longrightarrow Cd^{106} + ?$
(*iv*) $_5B^{10} + _2He^4 \longrightarrow _7N_{13} + ?$

Ans. (*i*) $_1H^1$, (*ii*) $_{28}Ni^{64}$ (*iii*) β^- (*iv*) $_0n^1$.

7. (*a*) Explain the difference between nuclear fission and nuclear fusion.

(*b*) It is proposed to use the nuclear fusion reaction

$$2\,_1H^2 \longrightarrow _2He^4 + \text{energy}$$

to produce industrial electric power. If the product is to be 50,000 kilowatts and the energy of the above reaction is used with 30 per cent efficiency, how many grams of deuterium fuel will be needed per day?

Ans. 25 gms.

8. By natural radioactivity, U^{238} emits an α-particle. The heavy residual nucleus is called UX_1. UX_1 in turn emits a β-particle. The heavy residual nucleus from this radioactive process is called UX_2. Determine the atomic numbers and mass numbers of (*a*) UX_1 and (*b*) UX_2.

Ans. (*a*) 90, 234 ; (*b*) 91, 234.

9. Explain the principle of Aston's mass-spectrograph. Discuss its use (*a*) in determining the molecule weights of the isotopes, (*b*) in determining the relative abundance of the isotopes.

10. Magnesium has three naturally occurring isotopes with isotopic mass and relative abundance of 23.98 (78.60 per cent), 24.98 (10.11 per cent), and 25.98 (11.29 per cent). Find the true mass of the isotopic mixture.

Ans. 24.31

11. In the following incomplete nuclear equation,

$$_{29}Cu^{64} \longrightarrow ? + _{28}Ni^{64},$$

the missing term is

(*a*) an electron (*b*) a positron

(*c*) a neutron (*d*) a proton

Ans. (*b*).

12. Assuming equal weight of radioactive elements, the most dangrous to approach immediately would be one having a half-life of

(*a*) 0.001 minute (*b*) 4.5 billion years

(*c*) 12 days (*d*) 65 years.

Ans. (*a*)

13. Element 102, with a mass number of 353 was synthesised by bombarding $_{96}Cm^{240}$ with a single nuclear particle which it captured. The par icle used was which one of the following?

(*a*) $_{12}X^{13}$ (*b*) $_{13}X^{6}$ (*c*) $_{6}X^{13}$ (*d*) $_{13}X^{12}$

Ans. (*c*)

14. Through radio active decay, $_{92}U^{234}$ may be transformed into $_{72}Pb^{206}$.

This process involves the loss of

(*a*) 8 Alpha particles and 6 electrons

(*b*) 7 Alpha particles and 4 electrons

(*c*) 6 Alpha particles. 1 neutron and 3 protons.

(*d*) 6 Alpha particles, 3 electrons and 2 deutrons.

Ans. (*b*)

15. The break up of a nucleus of an atom into two nuclei medium weight is called

(*a*) Fission (*b*) Natural radioactivity (*c*) Fusion

(*d*) Artificial radioactivity.

Ans. (*a*)

16. The graphite rods in the nuclear pite

(*a*) convert fast moving neutrons into thermal neutrons

(*b*) react with U^{235} to release energy

(*c*) furnish deutrons to fission U^{238}

(*d*) undergo combustion which triggers the fission reaction.

Ans. (*a*)

17. One of the following is fissionable

(*a*) H−3 (*b*) Co−60 (*c*) He−4 (*d*) Pu−239

Ans. (*d*)

18. Radioactive changes differ from ordinary chemical changes in that radioactive changes:

(*a*) are explosive (*b*) absorb energy (*c*) release energy

(*d*) involve changes in the nucleus.

Ans. (*c*)

19. Which of the following materials is used for control rods in uranium reactions?

(*a*) titanium (*b*) antimony (*c*) carbon steel (*d*) boron steel.

Ans. (*d*)

20. Write notes on the following:

(*a*) Radioactive series
(*b*) Structure of nucleus
(*c*) Separation of isotopes
(*d*) Uses of radioactive isotopes.

Chapter 24

PHOTOCHEMISTRY

24.1. INTRODUCTION

The first importance of photochemistry as a branch of science lies principally in the fact that it provides the chemical potential which is necessary for biological chemistry to operate. From its earliest biological stages, the chemical origins of life were almost certainly photochemical reactions and the food and fuel of life, today is provided by photosynthesis. The discovery of laser has further helped in the growth of photochemistry. Earlier we have seen that in order to initiate a chemical reaction, the reactant molecules must overcome an energy barrier. The energy required to break the chemical bonds involved in the reaction is usually supplied in the form of thermal energy. However, other forms of energy, such as light and sound, have also been used to initiate chemical reactions. The branch of chemistry which deals with the study of chemical reactions produced directly or indirectly by light is called *Photochemistry*. Here we are mainly concerned with the radiation lying in visible and ultra-violet regions, *i.e.*, the wavelength range between 1000 Å to 2000 Å. Photochemical reactions receive their activation by the absorption of photons of light molecules. Radiation chemistry comprises the study of chemical effects produced by ionizing radiations. The term ionizing radiations includes alpha, beta, gamma and X-rays. There are many types of reactions which are brought about by exposure to light, such as oxidation, reduction, synthesis and polymerisation reactions.

24.2. THE ABSORPTION OF LIGHT

When a beam of monochromatic radiation falls upon a system, it can be transmitted, refracted, scattered or absorbed. Grothuss and Draper in 1818 established a relationship between the light absorbed and the chemical change occurring in a photochemical reaction. According to this law, "only the light that is absorbed by a substance is effective in producing a photochemical change." This is also sometimes referred to as the principle of photochemical activation. The converse of the law is not true. All absorbed light does not bring about chemical action. For example, light is strongly absorbed by solutions of potassium permanganate, but no chemical effect is produced. The fraction of the incident light absorbed by a homogeneous medium depends on the depth or the thickness of the medium. This is known as *Lambert's Law* which states that when a beam of monochromatic radiation passes through a homogeneous absorbing medium, equal fractions of the incident radiation are absorbed by successive layers of equal thickness of the light absorbing substance. It can be expressed as

coefficient
$$-\frac{dI}{I}=a.dx \qquad \ldots (24.1)$$

where I is the intensity of light and x is the thickness of the medium, a is called the absorption coefficient. On integration, equation (24.1) gives

$$I=I_0e^{-ax} \qquad \ldots (24.2)$$

with the boundary condition $I=I_0$ at $x=0$. The intensity I_a, of the light absorbed is given by

$$I_a=I_0-I$$
$$I_a=I_0-I_0e^{-ax}$$

or
$$I_a=I_0\,(1-e^{-ax}) \qquad \ldots (24.3)$$

When the absorbing medium is solution or gas, the relationship between the intensities of the incident and transmitted radiations is given by *Beer's Law*, which states that equal fractions of the incident radiation are absorbed by equal changes in concentration of the absorbing substance in a path of constant length; that is,

$$I_a=I_0e^{-\varepsilon cx} \qquad \ldots (24.4)$$

where c is the molar concentration and ϵ is the molar extinction coefficient. The amount of light absorbed is

$$I_a=I_0-I$$
$$=I_0\,(1-e^{-\varepsilon cx}) \qquad \ldots (24.5)$$

The Beer's law is valid only in dilute solution and when monochromatic light is used. The extinction coefficient ϵ varies a great deal from substance to substance and also with the wave-length of the light used. The nature and position of the absorption band determines the colour of the substance.

24.3. THE LAW OF PHOTOCHEMICAL EQUIVALENCE

A. Einstein in 1912 applied the concept of the quantum of energy to photochemical reactions of molecules. This law, sometimss called the law of photochemical equivalence or the principle of quantum activation states: *Each quantum of radiation absorbed by a molecule activates one molecule in the primary step of photochemical process.*

The energy E absorbed per mole in a photochemical process is given by

$$E=Nh\nu \qquad \ldots (24.6)$$

where ν is the frequency of the absorbed radiation, h is Planck's constant and N is the Avogadro's Number. Since ν is equal to c/λ, where c is the velocity of light and λ is the wave length in cm, equation (24.6) can now be written as,

$$E=\frac{Nhc}{\lambda}\text{ ergs mole}^{-1} \qquad \ldots (24.7)$$

Substituting the numerical values for N, h and c we get,

$$E=\frac{6.025\times10^{23}\times6.625\times10^{-27}\times2.998\times10^{10}}{\lambda}$$

$$=\frac{1.196\times10^{16}}{\lambda}\text{ ergs mole}^{-1}$$

or

$$E=\frac{2.859}{\lambda}\times10^{5}\text{ kcal mol}^{-1} \qquad \ldots (24.8)$$

The quantity E defined by (24.7) is called one *einstein* of radiation of the given wavelength λ. It can be seen from this equation that the energy absorbed per mole decreases as the wave-length increases. In other words, the value of energy is inversely proportional to the wavelength of the light absorbed.

24.4. THE QUANTUM YIELD OR EFFICIENCY

The law of photochemical equivalence is applicable only to primary photochemicals process i.e., when as a result of absorption of light, only one molecule decomposes and the products enter no further reaction. The Einstein law is usually marked by secondary reactions and radiative and non-radiative transitions which prevent a simple 1 : 1 relationship between the number of photons absorbed and the number of molecules of final products in the reaction. The results of photochemical process are frequently expressed in terms of the *quantum yield* or *quantum efficiency* of the reaction. It is the number of moles of reactant consumed or product formed for each einstein of absorbed radiation. The quantity is defined as

$$\text{Quantum yield } \phi=\frac{\text{Number of moles reacting}}{\text{Number of einsteins absorbed}} \qquad \ldots (24.9)$$

An experimental arrangement for a photochemical study is shown in Fig. 24.1. The light from the source passes through a monochromotor which yields light of definite wavelength (λ). The light from a monochromotor enters a reaction cell filled with the reaction mixture. The part of light which is not absorbed strikes the detector, mostly a thermopile. The intensity of light is measured with the empty cell and with a reaction mixture.

Photo-electric cell also be used as detectors, but they must be calibrated for each frequency. Chemical actinometers are often used to measure the intensity of light radiation. It utilises a chemical reaction which has been accurately investigated in its photochemical behaviour. One of the most reproducible reactions is the decomposition of oxalic acid in presence of uranyl sulphate. The reaction can be written as

$$UO_2 + h\nu \longrightarrow (UO_2^{++})^*$$

$$(UO_2^{++})^* + (COOH)_2 \longrightarrow UO_2^{++} + CO_2 + CO + H_2O$$

The oxalic acid concentration can be determined by titration with permanganate. This reaction has a quantum yield of 0.50. It has been found that the law of photochemical equivalence applies only to the primary process of the reaction since only in a few cases the quantum yield is unity as required by the law of the photo-chemical equivalence. The values of quantum yields range from almost zero to very large values, e.g. 10^5.

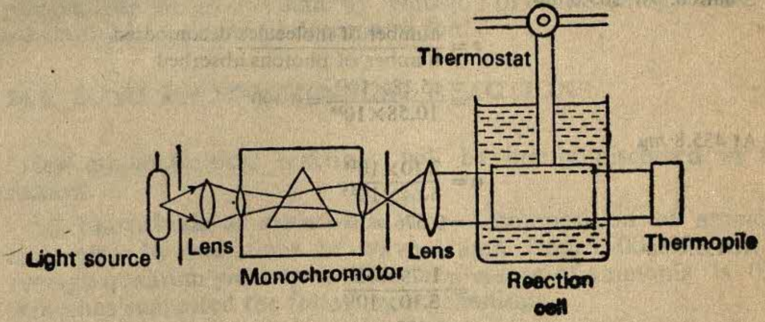


Fig. 24.1. Arrangement for photochemical studies.

Problem. 24.1. In the photobromination of cinnamic acid to dibromocinnamic acid, using light of wavelength 4358 at 30.6°, a light intensity of 14,000 ergs sec^{-1} produced a decrease of 0.075 millimole of bromine during an exposure of 1105 sec. The solution absorbed 80.1 per cent of the light passing through it. Calculate the quantum yield.

Solution. $E = h\nu = \frac{hc}{\lambda}$

$$= (6.62\times20^{-27})(3\times10^{10})(4.358\times10^{-5})$$

$$= 4.54\times10^{-12} \text{ erg per quantum}$$

$$\text{Number of quanta absorbed} = \frac{(14.000)(0.801)(1105)}{4.54\times10^{-12}}$$

$$= 2.74\times10^{18}$$

$$\text{Number of molecules of } Br_3 \text{ reacting} = (7.5\times10^{-5})(6.02\times10^{23})$$

$$= 45.2\times10^{18}$$

$$\text{Quantum effieiency } (\phi) = \frac{45.2\times10^{8}}{2.74\times10^{18}} = 16.5.$$

Problem. 24.2. From the following data for the uranyl oxalate system, evaluate the quantum efficiency at each wave length.

Wave length $m\mu$	*Fraction of oxalate decomposed*	*Molecules decomposed* $\times 10^{18}$	*Photons absorbed* $\times 10^{-13}$
365.5	0.0592	5.18	10.58
435.8	0.0242	2.10	3.64
435.8	0.0208	1.79	3.10

Solution. At 365.5 $m\mu$

$$\phi = \frac{\text{number of molecules decomposed}}{\text{number of photons absorbed}}$$

$$= \frac{5.18 \times 10^{18}}{10.58 \times 10^{18}} = 0.490$$

At 435.8 $m\mu$

$$\phi = \frac{2.10 \times 10^{18}}{3.64 \times 10^{18}}$$

$$= 0.576$$

At 435.8 $m\mu$

$$= \frac{1.79 \times 10^{18}}{3.10 \times 10^{18}}$$

$$= 0.577$$

24.5. PHOTOCHEMICAL PROCESSES

All photo-chemical processes can broadly be classified into two types: (*a*) The primary process and (*b*) The secondary process.

The primary process. As a first step, a photochemical reaction requires absorption of energy. The molecule is thus raised to a higher energy level. This can lead to four different types of behaviour as shown in Fig. 24.2. In Type I, transition is from a stable-ground state to a stable excited state. The corresponding spectrum consists of discontinuous bands with a fine structure of closely packed lines as shown. Type II represents a transition to an unstable state which immediately undergoes disassociation. Type III also leads to dissociation because the energy level reached lies

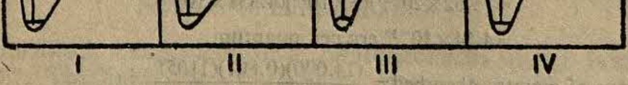


Fig. 24.2. Primary photo-chemical processes.

above the binding energy of the molecule. Type IV is a combination of type II and type III. The initial transition is from one stable state to another but, the upper state is intersected by the potential energy surface of an unstable state. When the molecule is vibrating in the excited state, as soon as it reaches a point where the two curves cross, it undergoes dissociation. This type of behaviour is referred to as predissociation.

The secondary process. This process involves the excited atoms, molecules or free radicals. A large number of paths are available to a molecule, some of them may lead to the return of the molecule to the ground state by emission of excess energy while the others produce chemical decomposition.

24.6. SOME PHOTOCHEMICAL REACTIONS

A few photochemical reactions will be briefly discussed in this section.

(*a*) **Photolysis of ammonia.** The decomposition of ammonia takes place by radiations of wave length from 1600-2000 Å. The average quantum yield up to 500 mm pressure of ammonia is 0.25. Wing has suggested the following mechanism:

$$NH_3+h\nu \longrightarrow NH_2+H \text{ (primary process)} \quad \ldots (i)$$
$$NH_2+H \longrightarrow NH_3 \quad \ldots (ii)$$
$$H+H \longrightarrow H_2 \quad \ldots (iii)$$
$$NH_2+NH_2 \longrightarrow N_2H_4 \quad \ldots (iv)$$
$$N_2H_4+H \longrightarrow NH_3+NH_2 \quad \ldots (v)$$
$$NH_2+NH_2 \longrightarrow N_2+2H_2 \quad \ldots (vi)$$

The low observed quantum yield may be due to the fact that the products of the primary stage NH_2 and H recombine to form ammonia.

(*b*) **Decomposition of hydrogen iodide in the gaseous phase.** From the studies of molecular spectra, it is clear that one molecule of HI absorbs light of wave length less than 4.000 Å, the molecule dissociates into an atom of hydrogen and an atom of iodine, the latter is in the excited state. The reaction has been extensively studied by E. Warburg.

The primary process of the reaction is therefore

$$HI \xrightarrow{h\nu} H+I^*$$

The possible secondary processes that follow this step are:

$$HI+H \longrightarrow H_2+I \quad \ldots (i)$$
$$I+HI \longrightarrow I_2+H \quad \ldots (ii)$$
$$H+H \longrightarrow H_2 \quad \ldots (iii)$$

$$I+I \longrightarrow I_2 \qquad \ldots (iv)$$

$$I+H \longrightarrow HI \qquad \ldots (v)$$

In the above reactions, (*iii*) and (*v*) are highly exothermic with the result that the products in both cases have such high energies that they will immediately dissociate unless the reaction has taken place in the presence of third atom. Such three body collisions are however, unlikely. Reaction (*ii*) is an endothermic process and therefore takes place slowly. The elimination of these three reactions leave reactions (*i*) and (*iv*) as the likely secondary processes. The decomposition of HI can now be written as consisting of a primary and two secondary processes:

$$HI \xrightarrow{h\nu} H+I^*$$

$$HI+H \longrightarrow H_2+I$$

$$I+I \longrightarrow I_2$$

On adding these three equations, we get:

$$2HI \xrightarrow{h\nu} H_2+I_2$$

Thus the absorption of one quantum of radiation leads to the decomposition of two hydrogen iodide molecules. This agrees with the measured quantum efficiency.

(*c*) **The hydrogen-chlorine reaction**. If a mixture of hydrogen and chlorine is exposed to visible or ultra-violet light of wave length less than 4800 Å, a fast reaction occurs resulting in the formation of hydrogen chloride. The first step involves the dissociation of chlorine molecule and is followed by other fast steps:

$$Cl_2+h\nu \longrightarrow 2Cl \qquad \ldots (i)$$

$$Cl+H_2 \longrightarrow HCl+H \qquad \ldots (ii)$$

$$H+Cl_2 \longrightarrow HCl+Cl \qquad \ldots (iii)$$

$$Cl \text{ (at walls)} \longrightarrow \tfrac{1}{2} Cl_2 \qquad \ldots (iv)$$

The quantum yield of the reaction is exceptionally high (10^4 to 10^6). Once the reaction has been started by the absorption of one quantum of light, a very large number of hydrogen chloride molecules are formed as a result of the continued repetition of steps (*ii*) and (*iii*) of reactions. The chain is only terminated at the walls of the reaction vessel.

(*d*) **Dimerization of anthracene in solution**. When anthracene in benzene solution is exposed to U.V. light, dimerization occurs and dianthracene is formed.

$$2C_{14}H_{10}+h\nu \longrightarrow C_{28}H_{20}$$

In dilute solution, the reaction is accompanied by fluorescence and the quantum efficiency is small, but as the concentration is increased, the fluorescence falls off whereas the efficiency increases towards a limiting value. When the latter is attained, there is very little fluorescence. The results can be shown quantitatively by the curves in Fig. 24.3.

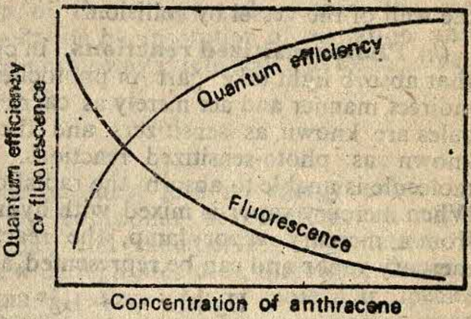


Fig. 24.3. Dimerization of anthracene.

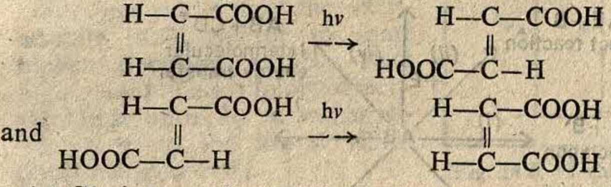
(*e*) **Double decomposition**. Hexahydrobenzene, in the presence of bromine, illuminated by light of wave length 4760 Å, gives monobromohexahydrobenzene and hydrogen bromide.

$$C_6H_{12}+Br_2 \xrightarrow{h\nu} C_6H_{11}Br+HBr$$

The photochemical hydrolysis of monochloroacetic acid is another example of such a reaction,

$$CH_2Cl.COOH+H_2O \xrightarrow{h\nu} CH_2(OH)COOH+HCl$$

(*f*) **Isomeric transformation.** Some substances, when photolysed, are transformed to the isomeric form, such as conversion of maleic acid into fumaric acid and the reverse reaction, by exposing their aqueous solutions to light of wave length 2070 Å, 2530 Å and 2820 Å.



$$\begin{array}{c}H-C-COOH\\ \|\\ H-C-COOH\end{array} \xrightarrow{h\nu} \begin{array}{c}H-C-COOH\\ \|\\ HOOC-C-H\end{array}$$

and

$$\begin{array}{c}H-C-COOH\\ \|\\ HOOC-C-H\end{array} \xrightarrow{h\nu} \begin{array}{c}H-C-COOH\\ \|\\ H-C-COOH\end{array}$$

(*g*) **Chain reactions.** There are many instances where a single molecule dissociates and one of the fragments reacts in such a way that a chain of dissociation results. The combination of hydrogen and chlorine is a common example which proceeds as under:

$$Cl_2+h\nu \longrightarrow 2Cl$$
$$Cl+H_2 \longrightarrow HCl+H$$
$$H+Cl_2 \longrightarrow HCl+Cl$$

Such a chain continues until the free atoms unite, thus terminating the chain. $H+Cl \longrightarrow HCl.$

Once the free atoms with excess energy are produced by the photon, the chain continues until the energy is diverted to other location where it no longer acts as a dissociating agent. Thus the termination reaction above does not take place instantaneously or to the wall of the vessel by collision.

(*h*) **Photosensitized reactions.** In certain cases, the molecules that absorb light take part in photochemical reaction only in an indirect manner and act merely as carriers of energy. Such molecules are known as sensitizers and the process of this type are known as photo-sensitized reactions. For example, a hydrogen molecule is unable to absorb the radiation of wave length 2537 Å. When mercury vapor is mixed with hydrogen and exposed to light from a mercury vapor lamp, the reaction is photo-sensitized by mercury vapor and can be represented as:

$$Hg + h\nu \longrightarrow Hg^*$$
$$Hg^* + H_2 \longrightarrow Hg + 2H$$

where Hg* represents an activated mercury atom. The most important example of photosensitization is the action of chlorophyll in the combination of carbon dioxide and water in presence of sun light. The process is known as photo-synthesis (see. Sec. 24.8).

24.7. PHOTO PROCESS

Luminescence the emission of radiation from excited species is one of the several paths by which the excess energy may be lost as shown in Fig. 24.4. The general phenomenon of light emission from electronically excited species is known as luminescence. Luminescent emission provides some of the most reliable information about the nature of primary photochemical processes. Competition exists between emission and other factors of excited species (quenching, reaction, decomposition, etc.) and the dependence of emission intensity on temperature, reactant concentrations, and so on, may

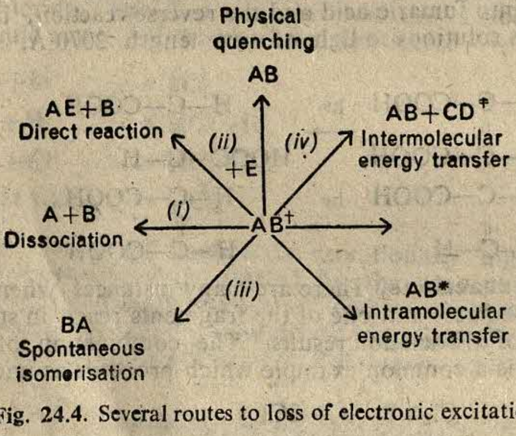


Fig. 24.4. Several routes to loss of electronic excitation.

yield valuable information about nature and efficiencies of various processes.

The various individual luminescent phenomena are named according to the mode of excitation of the energy rich species. We are concerned primarily with excitation by absorption of radiation and emission from species excited in this way is referred to as fluorescence or phosphorescence.

Fluorescence

An electronically excited atom must lose its energy either by emission of radiation or by collisional deactivation; chemical decomposition is not possible, and radiationless degradation is extremely improbable. At low enough pressures, therefore, fluorescent emission is expected from all atoms. Many molecular species however either, do not exhibit fluorescence or fluoresce weakly even when bimolecular reaction or physical deactivation does not occur. Some general principles can suggest whether a polyatomic organic molecule is likely to be strongly fluorescent. First absorption must occur at a wavelength long enough to ensure that chemical dissociation does not take place. Absorption to an instable state is clearly very unlikely to result in fluorescence. Secondly, intramolecular energy transfer must be relatively slow compared to the rate of radiation.

The explanation of fluorescence and phosphorescence can be best understood from a study of Fig. 24.5, this represents the one-electron excitation process. The absorption of light $h\nu_A$ by the ground-state molecule leads to promotion of one electron from a ground state M.O. to one of the vibrational sublevels of the excited-state M.O., S_1 (or to some higher electronic excited, state S_2, S_3 etc.) This rapidly deactivates in solution, by a radiationless process to the lowest vibrational sublevel of S_1.

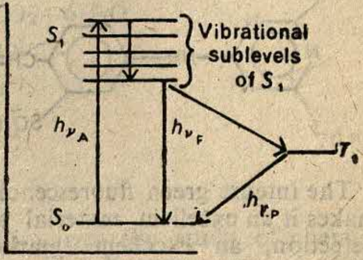


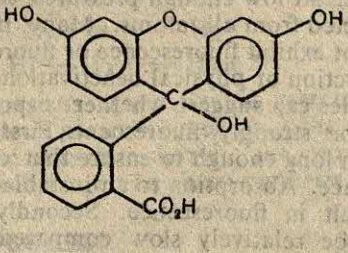
Fig. 24.5. Mechanism of Fluorescence and Phosphorescence.

For the electron to return from S_1 to the ground state, it must emit radiation ($h\nu_F$) which is clearly of lower energy and thus of longer wavelength than $h\nu_A$: the fluorescent radiation corresponds to $h\nu_F$.

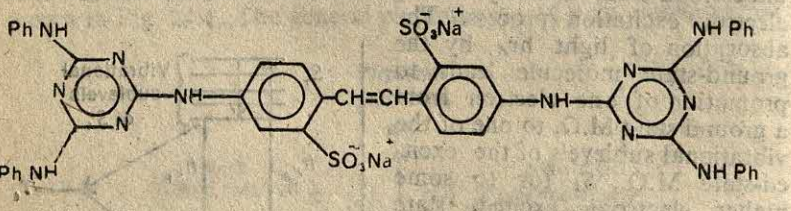
An alternative path involves loss of energy from S_1 to T_1; the principal difference between S_1 and T_1 is the electron spin orientation.

The two electrons originally occupying the groundstate M.O. under consideration, their spins must be antiparallel from the Pauli's exclusion principle. The excitation followed by the decay to the lowest vibrational level of S_1 does not alter the spin of the promoted electron, but the transition S_1 to T_1 does. Energy states containing only spin paired electrons are called singlet states (S_0, S_1, S_2) and those energy states containing parallel spin electrons are called triplet states (T_1, . . .) etc. Triplet states are more stable than singlet states and are longer lived, as they survive after the exciting radiation has been removed. These then decay to S_0 and in doing so emit radiation $h\nu_P$, called phosphorescent radiation. This has been explained in Fig. 24.5.

Important uses of fluorescence phenomenon are represented by the molecules of fluorescein and the optical 'brightner' derivative of 4, 4' diaminostilbene.



Florescein (acid form)



The intense green fluorescence of aqueous fluorescein solutions makes it an excellent material to add to water systems for leak detection, an excellent 'marker' for sea rescue operations etc. Minute quantities of optical brightners are added to detergents and are retained on the fabrics after washing in sunlight they fluoresce blue and add brightness to the fabrics after washing. Other applications of fluorescence depend on its extremely low detection limit, it is used in polymer chemistry to detect and identify plasticisers, and in the study of impurities. Fluorescent material dissolved in solution or in solid plastic bases can also detect radioactive decay, this forms the basis of scientallation counting of β-emitters etc. The three dimensional structure of proteins can be studied by measuring the proximity of known fluorescent group within the protein, these fluorescent groups can be either aromatic amino acids.

In addition to this fluorescence find wider applications in testing the conditions of food stuffs, for detecting ring worm. Fluorescent tubes are used for lighting purposes. The great importance of photo chemistry as a branch of science lies principally in the fact that it provides the chemical potential which is necessary for biological chemistry to operate. From its earliest abiological stages, the chemical origin of life were almost certainly photochemical reactions and the food and fuel of life today is provided by photosynthesis. The discovery of laser has further helped in the growth of photochemistry.

Solar Energy Conversion. The need to find a substitute for dwindling reserves of fossil fuels is becoming increasingly apparent. The power from nuclear emission is becoming unpopular because of the anxieties about the control of reactors and protection of their waste products. Nuclear power offers the prospects of almost unlimited energy supply if the formidable technical difficulties can be overcome. Although tidal and geothermal energy could become locally important they cannot make a major contribution to global demands. By contrast solar energy is available everywhere and the total supply for outstrips man's requirements as the radiant energy reaching the earth's surface in one hour approximates to the global requirements for one year. At noon 1 m^2 of the Sahara desert receives about 1 kW of solar power. The efficiency with which the incident radiation can be converted into usable power will be one of the main factors determining the exploitation of solar energy where $C_6H_{12}O_6$ stands for the basic synthesis product of the reaction which has glucose structure. The combustion reaction, complementary to the above process, can be written:

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$$

$$\triangle S = 43.6 \text{ cal.deg.}^{-1} \text{ mole}^{-1}.$$

$$\triangle G^\circ = -686 \text{ kcal. mole}^{-1}.$$

$$\triangle \overset{\circ}{H} = -673 \text{ kcal. mole}^{-1}.$$

24.8. RADIATION CHEMISTRY

This is the branch of science which involves the study of chemical effects induced by ionizing radiations like X-rays, γ-rays, electrons, protons, α-particles and neutrons. This is similar to photochemistry with a slight difference in absorption process.

Comparison with photochemistry. Radiation chemistry differs from photochemistry in the following respects:

1. In case of photochemistry, the absorption process is more complicated. Here the radiation is usually monochromatic, whereas the radiations in radiation chemistry may or may not be monochromatic.

2. In photochemistry, one molecule absorbs one photon which at least initially produces excited state, but in case of radiation

chemistry, the absorption process passes through a spectrum of lower energy states. Thus many other molecules are ionized or excited by the initial quantum or particles.

3. The absorption in photochemistry is purely and highly specific even in dilute solutions. The radiations are absorbed by the solute, whereas in radiation-chemistry, the radiations of all energies may be absorbed by both the solute and the solvent as well.

4. In photochemistry, the excited states produced by absorption are distributed homogeneously in the system. The radiation chemistry involves the presence of uncharged species like radicals and atoms rather than ions, produced in the primary reactions.

A quantitative measure of these radiation induced effects is given by a quantity called *G* value of a reaction. It is defined as the number of molecules reacting per 100 electron volts of energy absorbed. This definition may be expressed in a slightly different manner. Since the absorption of 1 electron volt by a molecule is equivalent to *N* electron volts per mole where *N* is Avagadro's number and if *e* is the electronic charge, then *Ne* will be equal to one faraday or 96,500 coulombs. Hence *N* electron volts is equivalent to 96,500 volt coulombs or 23,06 cal. Hence *G* value gives the number of moles reacting per 2,306 kcal of energy absorbed. In actual practice *G* is a small number. Only a few moles react for the absorption of over 2000 kcal of energy from the radiation, whereas chemical reactions require about 50 kcal per mole. Thus only a small part of the radiation absorbed is utilised for chemical reactions and most of it is absorbed as heat. The decomposition of water by radiation, has been studied in detail, though the reaction mechanism has not been definitely established. The earliest detectable products are hydrogen and hydrogen peroxide and transient reactive species with properties to be expected from H atoms and OH radicals.

The reaction may be represented as

$H_2O \rightarrow$ Ions and excited molecules $\rightarrow H+OH$.

The symbol → is used to represent the absorption of ionizing radiation. The other reactions are

$$\dot{H}+\dot{H} \rightarrow H_2$$
$$OH+OH \rightarrow H_2O_2$$

There is also a possibility that H_2 and H_2O_2 are formed directly from two molecules of water. There are large number of possible paths this simple reaction can proceed. The calculation of *G* value for each probable step and the overall *G* value is compared with the experimental *G* value. This helps us to establish the path of a reaction.

24.9. APPLICATIONS OF RADIATION CHEMISTRY

The applications of this fascinating field range far and wide. Following are the main uses of radiation chemistry:

1. To study reaction mechanism by radiolysis of solids, gases and liquids.
2. Nitrogen fixation.
3. Polymerisation.
4. Food-preservation.
5. Sterilization.
6. Production of detergents.
7. Production of gammaxane ethyl bromides.
8. Gamma-gardens.
9. For medical purposes.
10. To study the different rocks.

Radio chemistry. Radio-chemistry is the branch of chemistry which studies the application of radioactivity to chemical problems.

PROBLEMS

1. State and explain Einstein's law of photo-chemical equivalence. If 10 per cent of the energy of 100 W incandescent bulb goes into visible light, having an average wave length of 6000Å, how many quanta of light are emitted per second?

Ans. 30×10^{19} quanta.

2: What do you understand by the term photochemical reaction? How does it differ from a chemical reaction?

3. Define and explain Einstein's Law of photochemical equivalence. What is meant by photochemical equilibrium?

4. Give an account of the various types of photo-processes, you know of.

5. State and explain the law of photochemical equivalence. How are the discrepancies between the Einstein's law and experimental results explained?

6. A 2-mm layer of pyrox glass will transmit 10% of incident radiation of 3000Å. What percentage of light of the same wavelength will be absorbed by a 1 mm layer of the glass?

Ans. 61.4%

7. What do you understand by the quantum yield of a photochemical reaction? What are the causes of high or low quantum yields?

8. A certain photochemical reaction requires an activation energy of 30,000 cal. mol^{-1}. To what values does this correspond in the following units? (*a*) ergs per molecule, (*b*) frequency of light, (*c*) wave-number, (*d*) wave-length in angstroms and (*e*) electron volts?

Ans. (*a*) 2.08×10^{-12} erg molecule^{-1}
(*b*) 3.14×10^{14} sec^{-1}
(*c*) 10,500 cm^{-1}
(*d*) 9520Å
(*e*) 1.30 eV.

9. Write explanatory notes on (*a*) Grotthus-Draper law, (*b*) Lambert's law and (*c*) Beer's law.

10. How do you account for the fact that, in the combination of hydrogen and chlorine by exposure to ultra-violet light, more than 10^5 molecules are formed per quantum of energy absorbed?

11. Irradiation of HI vapor with ultra-violet radiation of wave length 2,070 Å leads to the formation of H_2 and I_2. It has been observed that for every calorie of radiant energy that is obsorbed, 0.00184 g. of HI is decomposed. How many HI molecules were decomposed per quantum of observed radiation?

Ans. 2.0

12. In photochemical combination of H_2 (g) and Cl_2 (g), a quantum efficiency of about 1.0×10^6 is obtained with a wave length of 4800 Å. How many moles of HCl(g) would be produced under these conditions per calorie of radiant energy absorbed?

Ans. 33.6 moles

13. Give a brief account of the different types of chemical reactions brought about by the action of light, giving examples.

14. What do you understand by chemiluminescence? Give two examples.

15. Write notes on the following:

(*a*) Fluorescence.

(*b*) Photosensitized reactions.

(*c*) The Primary process.

(*d*) The Secondary process.

Chapter 25

PHYSICAL PROPERTIES AND CHEMICAL CONSTITUTION

25.1. INTRODUCTION

The problem of establishing the chemical constitution or structure of a molecule has two aspects:

(*a*) determination of the actual size of the molecule, *i.e.*, distances between the constituent atoms,

(*b*) arrangement of the atoms in the molecule, nature of the bond and the strength of the molecule.

Various physical methods have been employed for the purpose. However, there is no single procedure for establishing the structure of molecules. The choice of a method or methods is determined from the nature of the molecule under investigation.

In this chapter, we shall briefly discuss some of these properties and how they can be used to establish the structure of molecules.

25.2. MOLAR REFRACTION

This property is characteristic of both gaseous and liquid states. The molar refraction of a compound may be expressed as,

$$R_M=\left(\frac{n^2-1}{n^2+2}\right)\frac{M}{d} \qquad \ldots (25.1)$$

where n is the refractive index of the medium (*i.e.*, $n=\sin i/\sin r$), M is the molecular weight and d density of the medium.

Molar refraction is both an additive and constitutive property. In order to get comparable results, it is necessary, therefore, to use light of a fixed frequency. Generally, the yellow light of sodium *D* line is employed. The molar refraction values have been used to decide between the alternative structures of some organic compounds: the formula which gives a calculated molar refraction in best agreement with the experimental value is the correct structure.

Table 25.1 lists the values of molar refraction for D-line of sodium.

TABLE 25.1.
Molar refraction contributions

Carbon	0.418	Triple bond	2.398
Hydrogen	1.100	3-membered ring	0.710
Chlorine	5.967	4-membered ring	0.480
Bromine	8.865	Oxygen (in OH group, O−)	1.525
Iodine	13.9000	Oxygen in (CO group O=)	2.211
Double Bond	1.733		

Problem 25.1. Calculate the molar refraction of acetone at 20°C. The refractive index, *n*, of acetone is 1.3591 and the density is 0.7910 g cm^{-3} at 20°C. The molecular weight of acetone is 58.08.

Solution. The molar refraction R_M is given by

$$R_M=\left(\frac{n^2-1}{n^2+2}\right)\frac{M}{d}$$

$$RM=\frac{(1.3591)^2-1}{(1.3591)^2+2}\times\frac{58.08}{0.7910}$$

$$R_M=16.17 \text{ c.c.}$$

Problem 25.2. The molar refractions for $CH_3CH_2CH_2CH_3$, CH_3CH_2OH and CH_3OH are 20.6, 12.9 and 8.3 respectively. Calculate the molar refraction for $CH_3\ CH_2\ CH_2OH$.

Solution. Since molar refractions are additive, molar refraction for CH_2 group can be calculated as follows:

$$\begin{aligned} R_M\,(CH_2) &= R_M(CH_3CH_2OH)-R_M(CH_3OH)\\ &=12.9-8.3\\ &=4.6 \end{aligned}$$

$$\begin{aligned} RM(CH_3CH_2CH_2OH) &= R_m(CH_3CH_2OH)+2R_M(CH_2)\\ &=12.9+2\times4.6\\ &=22.1 \end{aligned}$$

25.3. PARACHOR

Macleod gave an equation relating the surface tension of a liquid to the density and its vapors at a given temperature. According to this equation, we have

$$\gamma=C(D-d)^4 \quad \ldots (25.2)$$

where *C* is a constant, *D* is the density of the liquid and *d* is the density of the vapor.

Equation (25.2) can also be written as:

$$\frac{\gamma^{1/4}}{D-d}=C^{1/4} \quad \ldots (25.3)$$

Multiplying both sides of this equation by *M*, we get,

$$\left(\frac{M}{D-d}\right)\gamma^{1/4}=MC^{1/4}=[P] \quad \ldots (25.4)$$

The constant [*P*] is called the parachor. Since $D>>>d$, *d* can be neglected. Hence equation (25.4) can be written as

$$\left(\frac{M}{D}\right)\gamma^{1/4}=[P] \qquad \dots (25.5)$$

The quantity $\left(\frac{M}{D}\right)$ is called the molar volume. Hence parachor may be taken as equal to the molar volume of the liquid when its surface tension is unity.

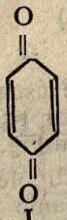
Parachor is both an additive and constitutive property and hence the parachor values can be used to decide the correct structure out of the different structures known for the given substances. The parachor values of some of the structural fragments are given in Table 25.2.

TABLE 25.2

Parachor values

Carbon	4.8	Double bond	23.2
Hydrogen	17.1	Triple bond	46.6
Oxygen	20.0	3-Ring	16.7
Nitrogen	12,5	4-Ring	11.6
Chlorine	53.8	5-Ring	8.5
		6-Ring	6.1
Bromine	68.0	Single bond	0.0

Two structural formulae has been proposed for quinones:



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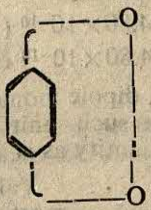


II

For structure I, we have

$$(6\times4.8)+(4\times17.1)+(2\times20.0)+(4\times23.2)+6.1$$
$$=236.1$$

For structure II:

$$(6\times4.8)+(4\times17.1)+(2\times20.0)+(3\times23.2)+(2\times6.1)$$
$$=219.0$$

The experimental value for quinone is 236.8. Structure I is thus a correct structure.

25.4. DIPOLE MOMENTS

When an electrically neutral molecule is placed in a uniform electric field, there is no net force tending to move the molecule. The field pulls the positive charges in the molecule in one direction and the negative charges in just the opposite direction, and the two forces cancel one another. If there is difference in electronegativity of the two atoms, then the more electronegative atom will carry the negative charge and the positive charge will be carried by the more electropositive atom. This results in the electrical dipole moment in the molecule.

The origin of dipole moment. In a heteronuclear molecule like HCl, each individual atom contributes one bonding electron. However, because chlorine is more electronegative than hydrogen, the valence electrons reside more within the influence of chlorine rather than hydrogen nucleus. Exact location is impossible in quantum mechanical language and the situation is simply represented by $H^{\delta+}-Cl^{\delta-}$. Such a bond constitutes a permanent electrical doublet or dipole μ.

The dipole moment of a molecule *AB* is defined as the distance between the centres of positive and negative charge, multiplied by the charge of one of them, *i.e.*,

$$\mu = qr \qquad \ldots (25.6)$$

where q is the charge and r is the distance between the centres of positive and negative charge.

The charges and distances are of the order of 10^{-10} esu and 10^{-8} cm (1Å) respectively. For one electron (charge 4.80×10^{-10} esu) separated from equally charged positive centre, by a distance of 1Å, the dipole moment would be

$$\begin{aligned}\mu &= 4.80 \times 10^{-10}\,(1 \times 10^{-8})\\ &= 4.80 \times 10^{-18} \text{ esu-cm.} \qquad \ldots (25.7)\end{aligned}$$

However rather than esu-cm, dipole moments are usually expressed in Debye units, where one such unit is equal to 10^{-10} esu-cm. Dipole moment is a vector quantity as is shown in Fig. 25.1.

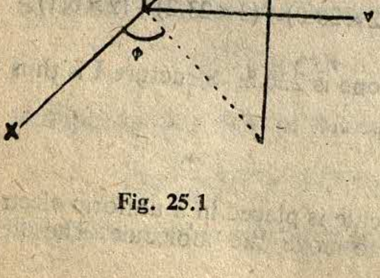


Fig. 25.1

Values of dipole moment for most inorganic compounds range from 0 to about 12, but some dyes have moments around 20 while proteins have been quoted at several hundred Debyes.

The magnitude of μ or bond polarity is crudely related to electronegativity differences of constituent atoms and their separation distances. There is of course no permanent charge displacement in homonuclear molecules like H_2 because both atoms are electronegatively identical and $\mu = 0$.

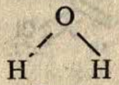
Molecules are, therefore of two types, *i.e.*, polar ($\mu > 0$) and non-polar ($\mu = 0$).

The observed dipole moment of a molecule is the vector sum of all the individual dipole moments. Carbon dioxide has a zero dipole moment since the molecule is symmetrical and linear, the vector sum of the bond moments being zero. The dipole moment of water is 1.85 D. This shows that the molecule is non-linear.

$O=C=O$

Carbon dioxide

I



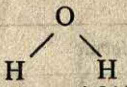
Water

II

In SI units q is measured in coulombs C, and r in meters, so μ is in cm. One Debye unit in SI units is equal to 3.336×10^{-30} cm.

The concept of bond moments and their vector addition is important from the point of view of determination of molecular structure since it is possible to deduce an unknown bond angle from the known bond moments and the experimentally determined bond dipole moment.

The bond angles thus obtained are however approximate. However the simplest and most reliable deductions which can be made about molecular structure from dipole moment measurements is whether a molecule is completely symmetrical or unsymmetrical, because the former case the dipole moment must be zero. Thus we have, for water and carbon dioxide molecule, following values of dipolemoments.



$\mu = 1.84$ D

$O=C=0$

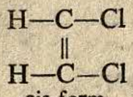
$\mu = 0$

Applications of dipole moment measurement We shall give some applications of dipole moment measurements in establishing the structure of the molecules.

(*a*) The absence of dipole moment in the molecule indicates that the electron pairs binding the atoms are situated equidistant between the constituents of the molecule.

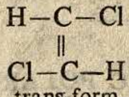
(*b*) The measurement of dipole moments in heteronuclear diatomic molecules is helpful in calculating the per cent ionic character.

(*c*) Dipole moments in certain cases are helpful in distinguishing between the cis- and trans-isomers. 1:2 dichloroethence exists as under



$$\begin{array}{c} H{-}C{-}Cl \\ \| \\ H{-}C{-}Cl \end{array}$$

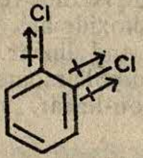
cis-form



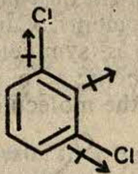
$$\begin{array}{c} H{-}C{-}Cl \\ \| \\ Cl{-}C{-}H \end{array}$$

trans-form

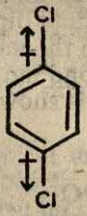
The cis-form has a dipole moment 1.90 *D* whereas the trans-isomer has a zero dipole moment. Other isomers which may be distinguished by dipole measurements are *o*−, *m*− and *p*− disubstituted benzenes.



μ=2.5D



μ=1.7D



μ=O

Certain atoms or groups *e.g.*, $-Cl$, $-NO_2$ when attached to a carbon atom with electrons and this end thus becomes the negative end of the dipole (−I effect). Other atoms or groups *i.e.*: $-CH_3$ attached to a carbon atom become the positive end of the dipole and are said to exert positive inductive effect (+I effect). The sign and the magnitude of the inductive effect are important in understanding chemical reactivity. The values of the dipole moments of some molecules are given in Table 25.3.

TABLE 25.3

Dipole moments of various molecules
(Debye units)

Molecule	*Dipole Moment*	*Molecule*	*Dipole Moment*
H_2, Cl_2, N_2	0.0	C_6H_6, naphthalene	0
CO_2, CS_2	0.0	CH_3OH	1.70
HCl	1.03	CH_3NH_2	1.24
HBr	0.78	CH_3COOH	1.74
HI	0.38	p-Dichlorobenzene	0
H_2O	1.84	o-Dichlorobenzene	2.50
HCN	2.93	p-Chloronitrobenzene	2.83
NH_3	1.46	m-chloronitrobenzene	3.73
CO	0.12		
PH_3	0.55		
PCl_3	0.78		
CH_3Cl	1.86		
CH_4, C_2H_6, C_2H_4, C_2H_2	0.0		

25.5. DIELECTRIC POLARIZATION

A molecule that possesses no permanent dipole can have a dipole moment induced when placed in an electric field. When a molecule is placed between two charged plates, then the nuclei which carry positive charge will be attracted toward the negative plate and the electrons toward the positive plate This causes polarization of the molecule and an electric dipole is formed. The polarization lasts as long as the field is applied. The molecule reverts to its original condition when the field is removed, this is called induced polarization. Figure 25.2 shows the polarization of a molecule in an electric field.

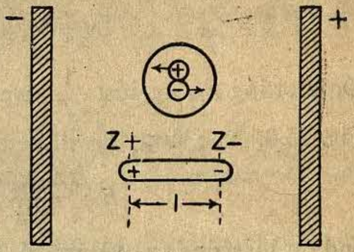


Fig. 25.2. Polarization of a molecule in an electric field.

The molar polarization which is the sum of the induced polarization (P_i) and the orientation polarization (P_0) is often described by the following equation:

$$P_M = \frac{4}{3}\pi N\alpha + \frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right) \qquad \ldots (25.8)$$

where N is the Avogadro's number, M is the molecular weight, α is the polarizability of the molecule, μ is the permanent dipole moment, k is a gas constant per molecule $\left(k=\frac{R}{N}\right)$and T is the temperature. The first term gives the contribution due to induced polarization

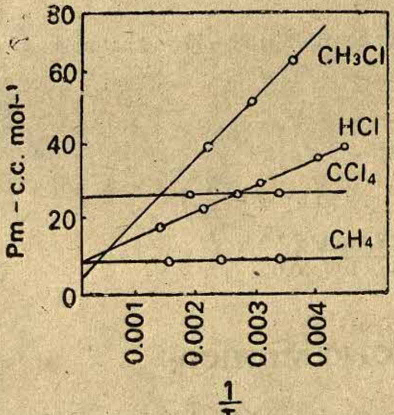


Fig. 25.3. Variation of total molar polarization with temperature.

and is constant represented by A. In the second term, all quantities are constant except T and hence can be represented as $\frac{B}{T}$. With these substitutions, equation (25.8) may be expressed as:

$$P_M = A + \frac{B}{T} \qquad \ldots (25.9)$$

On plotting P_M against $\frac{1}{T}$, we get a linear behaviour as shown in Fig. 25.3. The slope B will be equal to:

$$B = \frac{4\pi N\mu^2}{9k} \qquad \ldots (25.10)$$

and on inserting the values of N, μ and k we have,

$$\mu = 0.0128\sqrt{B} + 10^{-18} \qquad \ldots (25.11)$$

Problem 25.3. Given that

$P(\text{cc/mole}) = \frac{M}{\rho}\,\frac{D-1}{D+2} = \frac{4\pi N}{3}\left[\alpha + \frac{\mu^2}{3kT}\right]$ and that for CH_3Cl (g), P is 90.0 cc/mole at $\frac{1}{T} = 0.004$, and 50 cc/mole extrapolated to $\frac{1}{T} = 0.0$. Calculate α and μ for CH_3Cl.

Solution. At $\frac{1}{T} = 0$

$$P = \frac{4}{3}\pi N\alpha$$

$$50 = 4 \times \frac{22}{7} \times \frac{6.02 \times 10^{22}\alpha}{3}$$

$$\alpha = 1.98 \times 10^{-23} \text{ cc/molecule.}$$ **Ans.**

At $\frac{1}{T} = 0.00$

The second term in the equation is $90 - 50 = 40$ cc/mole,

$$\because \quad 40 = \frac{4\pi N\mu^2}{9kT}$$

$$\mu^2 = \frac{40 \times 9kT}{4\pi N}$$

$$\mu^2 = \frac{40 \times 9 \times RT}{4\pi N^2} \qquad \left(\because \; k = \frac{R}{N}\right)$$

$$= \frac{40 \times 9 \times 8.3 \times 10^7 \times 7}{4 \times 22 \times 36 \times 10^{46} \times 0.004}$$

$$\mu = 1.28 \text{ debyes}$$ **Ans.**

25.6. SPECTROSCOPIC METHODS

The word spectroscopy is widely used to mean the separation, detection and recording of energy changes (resonance peaks) involving nuclei, atoms or molecules. These changes are due to the emission absorption or scattering of electromagnetic radiation or particles. Spectrometry is that branch of physical sciences that treats the measurement of spectra.

According to the quantum theory of matter, the internal energy of a molecule may be raised by the absorption of a quantum of electromagnetic radiation if the energy of the quantum exactly equals the difference $\triangle E$ between two energy levels in the molecule, *i.e.*

$$\triangle E = h\nu = \frac{hc}{\lambda} \qquad \ldots (25.12)$$

where h is the Plank's constant, ν is the frequency, λ is the wave length of the electromagnetic radiation and c is the velocity of light in vacuum.

Molecules, like atoms, can exist in a number of states of differing energy and transitions in between them result in the absorption or emission of energy in the form of radiation of definite frequencies *i.e.*, a line spectrum of the molecule appears. A large number of such transitions are possible so that the resulting spectrum consists of several lines spaced so close together making a *band*. A typical band spectrum is shown in Fig. 25.4.

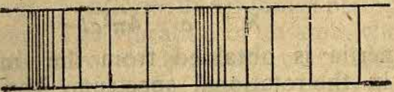


Fig. 25.4. A typical band spectrum.

The energy changes, which give rise to the spectrum, may consist of three types: (*a*) rotational, (*b*) vibrational, and (*c*) electronic excitation.

(*a*) **Rotational absorption spectra**. Pure rotational absorption spectra are observed in the far intra-red and microwave regions of the electromagnetic spectrum. The molecule must have a permanent dipole moment, before it can produce the rotational absorption spectra. Rotational energy levels are spaced close together with separations of ∼ 300 cal. The energies of the rotational levels of a diatomic molecule AB is given by

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \qquad \ldots (25.13)$$

where J is the rotational quantum number and I is the moment of inertia given by

$$I = \left(\frac{m_A m_B}{m_A + m_B} \right) / r^2_{AB} \qquad \ldots (25.14)$$

where m_A and m_B are the respective masses of the atoms and r_{AB} is the bond length. The term inside the brackets is called the reduced mass of the molecule and is denoted by μ. Transitions occur only between adjacent quantum levels, that is,

$$\triangle J = \pm 1$$

When a molecule is raised from one rotation level to another *i.e.*, from quantum number $J-1$ to the level J, the energy emitted is given by

$$h\nu = E_J - E_{(J-1)}$$

$$= \frac{h^2}{8\pi^2 I}\left[J(J+1) - J(J-1)\right]$$

$$= \frac{h^2}{4\pi^2 I}\,J$$

or
$$\nu = \frac{h}{4\pi^2 I}\,J \qquad \ldots (25.15)$$

From equation (25.15), it is clear that the spacing between the lines is equal to $\frac{h}{4\pi^2 I}$. In terms of wave number, we have

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{h}{4\pi^2 cI} \qquad \ldots (25.16)$$

The moment of inertia is obtained from the measured spacing between the lines in the rotational spectrum. The bond length r_{AB} can thus be determined for heteronuclear diatomic molecule from the knowledge of I and μ.

Problem 25.4. The vibrational frequency of HCl is 2989 cm^{-1} (in wave numbers). The isotopic weights are $H^1 = 1.008$ and $Cl^{35} = 35.97$ amu.

$(6.023 \times 10^{23}$ amu $= 1$ g$)$.

(*a*) Convert this frequency to $\sec^{-1}$.

(*b*) Calculate the reduced mass of the two atoms in HCl, in amu and in grams.

Solution. (*a*)
$$\frac{1}{\lambda} = 2989\ \text{cm}^{-1}$$

$$\nu = \frac{c}{\lambda} = 2.998 \times 10^{10}\ \text{cm sec}^{-1} \times 2989\ \text{cm}^{-1}$$

$$= 8.96 \times 10^{13}\ \text{sec}^{-1}.$$

(*b*)
$$\mu = \frac{m_A m_B}{m_A + m_B} = \frac{1.008 \times 34.97}{35.97} = 0.981\ \text{amu}.$$

and
$$\mu = \frac{0.981\ \text{amu} \times 1\text{g}}{6.023 \times 10^{23}\ \text{amu}} = 1.63 \times 10^{-24}\ \text{g}.$$

Problem. 25.5. The rotation spectrum of HCl vapor consists of a series of relatively even spaced lines when the chlorine is exclusively the ^{35}Cl isotope. The spacing between the two lines of the spectrum in terms of wavelength, is 4.7×10^{-2} cm. Calculate the bond length in HCl.

Solution. The difference in the frequency of any two adjacent rotational absorptions is equal to $2B$. The wavelength difference can be converted to a frequency difference,

$$2B = \Delta\nu = \frac{c}{\Delta\lambda}$$

$$= \frac{3.0 \times 10^{10}\ \text{cm s}^{-1}}{4.7 \times 10^{-2}\ \text{cm}}$$

$$= 3.2 \times 10^{11}\ \text{s}^{-1}$$

Since $$B=\frac{h}{8\pi^2 I}$$

$$I=\frac{6.6\times10^{-27}}{8\pi^2\times3.2\times10^{11}\ \mathrm{s}^{-1}}$$

$$=2.6\times10^{-40}\ \mathrm{erg{-}s^2}$$

For a diatomic molecule

$$I=\mu r_e^2$$

where γ_e is the internuclear separation at equilibrium

$$r_e^2=\frac{2.6\times10^{-40}\ \mathrm{erg\ s^2}}{\left(\frac{35\times1}{35+1}\bigg|6.02\times10^{23}\mathrm{g}\right)}$$

$$=1.61\times10^{-16}\ \mathrm{cm}$$

$$r_e=1.3\ \text{Å}$$

(*b*) **Vibrational spectra**. Atoms within molecules may vibrate about their average positions undergoing periodic displacements from these positions. The vibration of an atom with respect to other atoms in a molecule involves bending or stretching of the valence bonds which hold it. Vibrational spectra result from the changes in vibrational energy levels. All the vibrations of a molecule can be described as one or a combination of a certain number of fundamental modes of vibration Consider a molecule containing n atoms. The position of each atom can be defined by specifying the three coordinates *i.e.*, x, y and z cartesian coordinates. This will give rise to $3n$ number of coordinates. Since each coordinate value may be specified independently, a molecule of n atoms has $3n$ degrees of freedom. Once all $3n$ coordinates have been fixed, the bond distances and bond angles of the molecule are all fixed.

When a molecule is free to move in three dimensional space as a whole without change of shape, we can refer to such movement by noting the position of its centre of gravity at any instant and the position can be described if the values of its three coordinates is known. This translational motion uses 3 degrees of freedom and hence the remaining degrees of freedom will be $3n-3$. Similarly, the rotation of a non-linear molecule can be resolved into components about three perpendicular axes and this will require three degree of freedom. The molecule will now be left with $3n-6$ degrees of freedom.

∴ For a non-linear molecule, the number of fundamental vibrations $=3n-6$.

If the molecule is linear, there is no rotation about the bond axis, hence only two degrees of rotational freedom are required leaving $3n-5$ degrees of vibrational freedom. It can be shown from quantum mechanical considerations that the vibrational energy levels of a molecule are given by:

$$E=\left(v+\frac{1}{2}\right)h\nu_0 \qquad \ldots (25.17)$$

where v is the vibrational quantum number. The frequency v_0 of a diatomic molecule is related to mass m and force constant k by the equation:

$$v_0=\frac{1}{2\pi}\sqrt{\frac{k}{m}} \qquad \ldots (25.18)$$

The vibrational absorption spectrum of HCl is shown in Fig. 25.5.

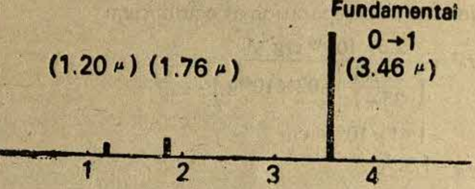


Fig. 25.5. Vibrational spectrum of HCl.

The strongest absorption band is at 3.46μ and a weak band at 1.76 μ and a much weaker band at 1.20μ.

Problem 25.6. Calculate the number of vibrations in the following molecules: (*a*) SO_2 (*b*) H_2 (*c*) CO_2.

Solution. (*a*) SO_2 is a non-linear molecule. The number of modes of vibration will be $3n-6$, where n is the number of atoms.

$$3n-6=3\times3-6=3 \text{ modes}$$

(*b*) Since H_2 is linear. There should be $3n-5=3\times2-5=1$ mode af vibration.

(*c*) CO_2 is a linear triatomic molecule. The modes of vibration will be

$$3n-5=3\times3-5=4 \text{ modes.}$$

Problem 25.7. Calculate the force constant for HCl^{35} from the fact that the fundamental vibration frequency is 8.667×10^{13} sec^{-1}.

The reduced mass of HCl is 1.628×10^{-24} gram.

Solution.

$$k=(2\pi v_0)^2\mu$$
$$=(2\times3.142\times8.667\times10^{13}\ \text{sec}^{-1})^2\,(1.628\times10^{-34}\ \text{g})$$
$$=4.81\times10^5 \text{ dynes cm}^{-1}.$$

Vibration-rotation spectra. Vibration-rotation spectra are exhibited by diatomic molecules with permanent dipole moments. Homonuclear diatomic molecules, such as O_2, Cl_2 or H_2, do not show vibration-rotation spectra since they do not have permanent dipoles. The exciting radiation can sometimes induce an oscillating dipole moment in a polyatomic molecule. For a vibrational transition from any level (quantum number v') to another level (quantum number v), the energy aborbed is given by

$$\triangle E_v=E_v-E_v'$$
$$\triangle E_v=(v+\tfrac{1}{2})\,hv_0-(v'+\tfrac{1}{2})hv_0$$
$$\triangle E_v=(v-v')hv_0 \qquad \ldots (25.19)$$

The accompanying vibrational transitions are superposed with rotational changes. The rotational changes add or subtract from

(25.19). The energy changes are given by

$$\triangle E = \triangle E_v + \triangle E_r \qquad \ldots (25.20)$$

Since,

$$\triangle E_r = \left(\frac{h^2}{4\pi^2 I} \right) J$$

$$\triangle E = (v - v') h\nu_0 \pm \left(\frac{h^2}{4\pi^2 I} \right) J \qquad \ldots (25.21)$$

Further

$$\triangle E = h\nu$$

$$\therefore \qquad h\nu = (v - v')\, h\nu_0 \pm \left(\frac{h^2}{4\pi^2 I} \right) J$$

or

$$\nu = (v - v')\nu_0 \pm \left(\frac{h}{4\pi^2 I} \right) J$$

$$= \triangle v\, \nu_0 \pm \left(\frac{h}{4\pi^2 I} \right) J \qquad \ldots (25.22)$$

where

$$\triangle v = v - v'$$

From (25.22), it follows that a line expected, corresponding to the vibration transition $\triangle v$, will be missing and instead there will be a pair of lines on either side of the expected position. This equation predicts equal spacing of vibration-rotation lines, but the actual spacings observed are variable. A typical vibration-rotation for HBr is shown in Fig. 25.6.

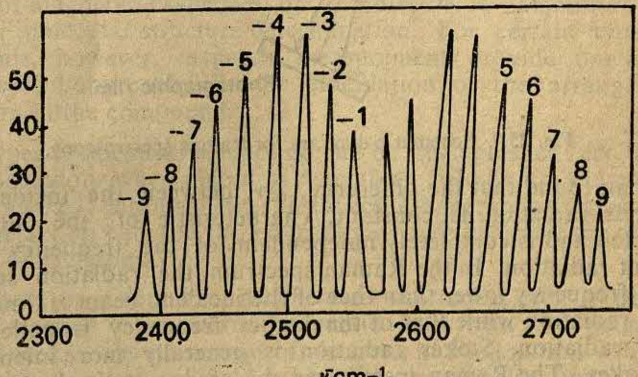


Fig. 25.6. Vibration-rotation spectrum of HBr for transition from $v=0$ to $v=1$.

25.7. RAMAN SPECTRA

When a beam of monochromatic visible or ultra-violet light is passed through a homogeneous medium, some light may be absorbed, some will be transmitted and some of it will be scattered. The scattered energy will consist almost entirely of radiation of the incident frequency. This is known as Rayleigh scattering, but in addition, certain, discrete frequencies above and below that of the incident beam will be scattered; this is referred to as Raman scattering.

The schematic arrangement for recording Raman spectrum is shown in Fig. 25.7.

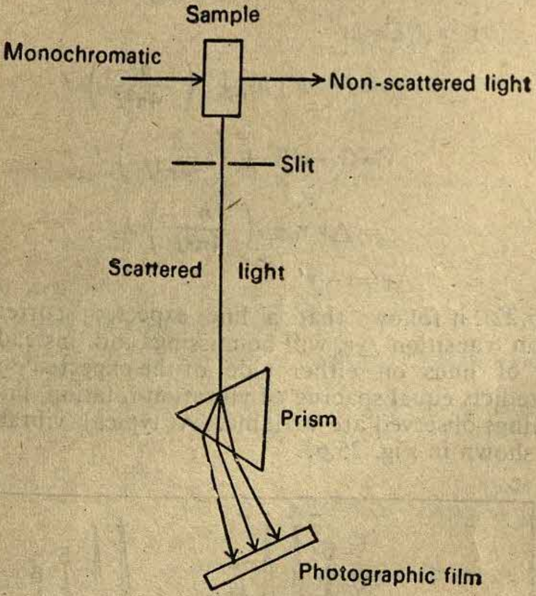


Fig. 25.7. Schematic diagram for Raman spectroscopy.

Raman found that the difference, $\triangle\nu$, between the incident and scattered radiation is constant, characteristic of the substance irradiated and is completely independent of the frequency of the incident radiation. In the Raman spectrum, the radiation scattered with a frequency lower than that of the incident beam is known as stokes radiation while that of the higher frequency is called anti-stokes radiation. Stokes radiation is generally more intense than anti-stokes. The Raman spectra can be used to study the vibration energy levels of molecules.

The differences between the frequencies of the scattered light and the frequency of the incident light correspond to transition between vibrational and rotational energy levels in the molecule. Thus Raman spectroscopy essentially provides the same kind of information as infrared spectroscopy with one important difference *i.e.*, a given molecular vibration will be Raman active only if there is a change in the polarizability of the molecule during the vibration. Qualitatively, it is associated with the deformation of electron cloud surrounding a molecule. The polarizability of a molecule will change during vibration if during vibration, the electron cloud become more compact or diffuse in going from one extreme vibrational configuration to another. The numbers of fundamental molecular vibrations which are infrared active or Raman active can be predicted for any molecular geometry. The proposed geometry of a molecule is confirmed by the agreement of its observed spectrum with the predicted spectrum. The Raman spectrum of chloroform is shown in Fig. 25.8.

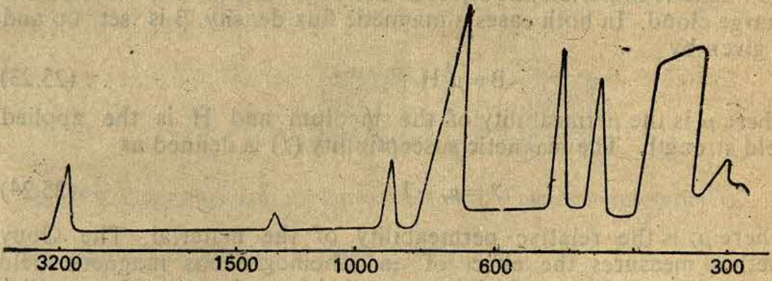


Fig. 25.8. Raman spectrum for CH_3Cl.

25.8. MAGNETIC PROPERTIES OF MOLECULES

A study of magnetic pryperties of a molecule is sometimes very useful for molecular structure determination. For certain types of compounds, however, magnetic measurements provide one of the most powerful approaches for the elucidation of the arrangement of electron in the compound.

Two types of chemical compound can be distinguished according to their behaviour when placed in a magnetic field *i.e.* (*i*) diamagnetic substances (*ii*) paramagnetic substances. Magnetism arises because of the interaction between the external magnetic field and the orbital electrons of the atoms.

Diamagnetism is found for all chemical substances and is caused by the interaction of an external magnetic field with the magnetic field produced by the movement of electrons in filled atomic orbitals. This results in an induced field which is directionally opposed to the applied field. Diamagnetism is independent of temperature but increases with atomic or molecular size and the diamagnetism of covalent compounds is approximately additive. However its effect is generally much smaller than that of paramagnetism.

Paramagnetism arises whenever an atom, ion or molecule possesses one or more unpaired electrons. The presence of these causes the element to behave like a small permanent magnet. An applied magnetic field tends to align all these magnets in parallel. This tendency is opposed by thermal effects which favour a random arrangement of the magnets. Paramagnetism is found in the compounds of the transition metals, due to the presence of unpaired of electrons in the lanthanoids and actinoids, due to the presence of f electrons, and a few molecules such as O_2, NO, NO_2 and ClO_2 which contain an odd number of valency electrons.

The Gouy Method of Measuring Magnetic Susceptibility

The application of a magnetic field to a paramagnetic substance causes magnetic dipoles to be lined up in the field direction; with diamagnetic materials the effect is one of polarization of the electron charge cloud. In both cases a magnetic flux density, β is set up and is given by

$$B = \mu H \qquad \ldots (25.23)$$

where μ is the permeability of the medium and H is the applied field strength. The magnetic susceptibility (χ) is defined as

$$\chi = \mu_r - 1 \qquad (25.24)$$

where μ_r is the relative permeability of the material. The Gouy method measures the effect of an inhomogeneous magnetic field upon the specimen, which is suspended from the arm of a sensitive balance by a fine silver chain. The specimen is in the form of a rod of uniform cross-sectional area (A) where each end of the rod is in a region of uniform magnetic field, in this case that outside the magnet (H_0) and that at the centre of the magnetic field (H). The magnetic susceptibility of the specimen is obtained from the relationship

$$F = \tfrac{1}{2}\mu_o A\chi\,(H^2 - H_o^2) \qquad \ldots (25.25)$$

The specimen, which may be crystalline or liquid is contained in a flat bottomed Gouy tube, constructed of glass, about 10-15 cm in length and of uniform cross-sectional diameter (3-10 mm). The tube itself, being a hollow specimen, experiences a force when the sample is weighed in the field. The measurements are also made in air, which has an appreciable susceptibility account must be taken of the volume of the air displaced. On taking these into consideration we get,

$$F = \tfrac{1}{2}\mu_0 A(\chi - \chi_a)\,(H^2 - H_o^2) + \delta \qquad \ldots (25.26)$$

where χ_a is the magnetic susceptibility of air and δ is the tube correction factor. Measurements are made, in and out of the magnetic field, which may be either that from a permanent magnet or an electromagnet, generally in the range 400 mT to 1T (T=tesla) and with a pole gap of 2-3 cm. To avoid measurements of the field strength, area of the specimen and other constant factors, a calibration is performed using a substance of known susceptibility, *e.g.* a standard nickel chloride solution or solid $HgCo(SCN)_4$. Powdered materials must be well packed in the tube to avoid errors from air blocks. The volume of the sample may be determined conveniently from the mass of a volume of water equal to that of the specimen volume.

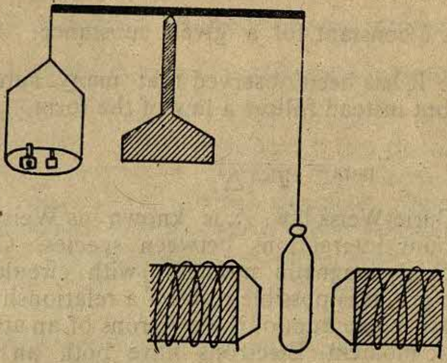


Fig. 25.9. Gouy apparatus for the measurement of magnetic susceptibility.

For a constant length specimen the term

$$\tfrac{1}{2}\mu_o A(H^2-H_o^2)$$

is a constant, *i.e.*

$$F'=(F-\delta)=C(\chi-\chi_o)$$

$$g\triangle m=C(\chi-\chi_o) \qquad \ldots (25.27)$$

where $\triangle m$ is the apparent change in mass on applying the magnetic field. Relation (25.27) can also be written as

$$g\triangle m=C\left(\frac{\chi_x{}^v\times m_s}{V}-\chi_a\right) \qquad \ldots (25.28)$$

where m_s=mass of the sample, V=sample volume, $\chi^v=\chi/\rho$ where ν is the specific volume. Further,

$$c'=\frac{gV}{C}=\frac{\chi^v\times m_s-\chi_a{}'V}{\triangle m}$$

or

$$\chi^v=\frac{c'\triangle m+\chi_a V}{m_s} \qquad \ldots (25.29)$$

An equation can be derived which relates the magnetic susceptibility, the magnetic polarisability, α_M and the permanent magnetic moment μ_M *i.e.*

$$\chi=M(\alpha_M+\mu_M{}^2/3kT) \qquad \ldots (25.30)$$

k is Boltzmann's constant and N is Avogadro's number. Measurement of χ as function of T helps in the evalution of α_M and μ_M. the first term deals with the magnetic contribution and second the paramagnetic contribution. It follows from the above that the paramagnetic contribution to the total susceptibility, χ_{para}, may be written in the form,

$$\chi_{\text{para}}=\frac{C}{T} \qquad \ldots (25.30a)$$

Since $\frac{\mu^2 M}{3kT}$ is a constant for a given substance. This is called Curie equation. It has been observed that many substances do not obey this law, but instead follow a law of the form,

$$\chi_{\text{para}}=\frac{C}{T-\Delta} \qquad \ldots (25.31)$$

known as the Curie-Weiss law. Δ is known as Weiss constant, this takes into account interactions between species. Classically it is possible to associate magnetic moments with circulating electrical charges. Therefore, it is possible to have a relationship between the resultant angular momentum of the electrons of an atom or molecule and its magnetic moment. Electrons have both an orbital angular momentum and a spin angular moment. Both of these can contribute to the observed magnetic moment, but we shall consider only cases where the spin contribution alone effectively decides the magnetic moment. The magnetic moment associated with one electron spin is 1.73 Bohr magnetons. (The Bohr magnetons $= he/4\pi$ mc or 9.273×10^{-21} erg gauss^{-1}).

The reactant magnetic moment for n unpaired electrons which occupy several different orbitals is

$$\mu_M=\sqrt{n(n+2)} \text{ Bohr magnestons} \qquad \ldots (25.32)$$

The magnetic moment of FeF_6 is 5.92 which corresponds to five unpaired electrons, whereas that of $Fe(CN)_6^{-3}$ complex should 1.73 Bohr magnetons (BM) corresponding to one unpaired electron. The magnetic moment measurement helps us to know the number of unpaired electrons and helps to elucidate the geometry of the transition metal compounds.

25.9. NUCLEAR MAGNETIC RESONANCE (NMR)

Nuclear magnetic resonance (NMR) technique is the most revolutionary of the spectroscopic methods now in use by chemists in all branches of the science. Like IR and UV spectroscopy the method is non-destructible one and permits the recovery of the sample for further evaluation.

As implied in the name, nuclear magnetic resonance is concerned with the magnetic properties of certain nuclei, notably the nucleus of the hydrogen atom—the proton. Studying an organic molecule by NMR spectroscopy enables us to record differences in the magnetic properties of the various nuclei present, and to deduce in large measure what are the positions of these nuclei within the molecule. We can for proton NMR deduce how many different kinds of hydrogen environments there are in the molecule, and also which hydrogen atoms are present an neighbouring carbon atoms. We can also measure how many hydrogen atoms are present in each of these environments.

Nuclei are characterised by nuclear spin quantum numbers, I, which have the values 1/2, 1, 3/2. . . expressed in units of $\frac{h}{2\pi}$. For a given nucleus with spin number I, there are $2I+1$ orientations possible in a magnetic field. It has been found that the nuclei with even atomic numbers and even mass numbers have zero nuclear spins. Such nuclei do not exhibit nuclear magnetic resonance. For the nuclei with even states $I=1/2$, there are two possible orientations, $[2(1/2)+1]$. The common examples of such nuclei are ^1H, ^{15}N, ^{19}F and ^{31}P. However very frequently we consider the hydrogen nuclei (^1H).

The proton behaves like a spinning magnet and it precesses like a top around the axis of an applied magnetic field and can do so in two principal orientations, either aligned with the field (low energy) or opposed to the field (high energy) as shown in Fig. 25.10, where B_0 is the external magnetic field. The spinning frequency of the nucleus does not change, but the speed of precession does. The precessional frequency, ν, is directly proportional to the strength of the external field B_0; that is

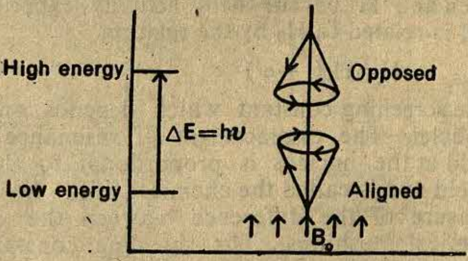


Fig. 25.10

$$\nu \propto B_0 \quad \ldots (25.33)$$

For example a proton when exposed to an external magnetic field of 1.4 T (≡14,000 gauss) will precess ≃60 million times per second, so that $\nu = 60$ MHz; in doing so it will take up one of two orientations with respect to the axis of the external field—aligned or opposed. If a proton is precessing in the aligned orientation, it can absorb energy and pass into the opposed orientation; subsequently it can lose this extra energy and relax back into the aligned position. If we irradiate the precessing nuclei with a beam of radio-frequency energy of the correct frequency, the low-energy nuclei may absorb this energy and move to a higher energy state. The precessing proton will only absorb energy from the radio-frequency source if the precessing frequency is the same as the frequency of the radio-frequency beam; when this occurs, the nucleus and the radio-frequency beam are said to be in resonance; hence the term nuclear magnetic resonance (n m r). In an applied magnetic field, magnetic nuclei like the proton precess at a frequency ν, which is proportional to the strength of the applied field. The exact frequency is given by

$$\nu = \mu\beta_N B_0/hI \qquad \ldots (25.34)$$

where B_0=strength of the applied external field

h=planck's constant

μ=magnetic moment of the particular nucleus

I=spin quantum number

β_N=nuclear magneton constant.

Chemical Shift

The field at a nucleus due to the field of the magnet is modified by the induced diamagnetic electronic currents. These set up a secondary magnetic field. Let H_0 be the magnetic field in the bulk of the specimen and H be the field actually experienced by the nuclei. The H is related to H_0 by the relation

$$H = H_0(1-\sigma') \qquad \ldots (25.35)$$

where σ' is the screening constant which depends on the environment of the nuclei. The displacement of resonance caused by the additional field at the nucleus is proportional to the strength of the applied field and is called the chemical shift. In fact, chemical shift is a measure of the difference between the σ' values for different chemical positions. The shielding constant σ may be defined as

$$\sigma = \sigma' \times 10^6 = \frac{H - H_{ref}}{H_{ref}} \times 10^6 \qquad \ldots (25.36)$$

where H is strength of the magnetic field at which resonance occurs and H_{ref} is the field at which the nucleus in reference surroundings gives resonance at the same frequency. Chemical shifts δ are given as

$$\delta = \sigma_1 - \sigma_{ref} = \frac{H - H_{ref}}{H_{ref}} \times 10^6 \qquad \ldots (25.37)$$

With protons a very convenient reference compound is, tetramethyl silane (TMS) and the quantity $\tau = 10 - \delta$ has been introduced so that

$$\tau\,(\text{ppm}) = 10 - \frac{\Delta\,(Me_4Si) \times 10^6}{\text{Oscillator frequency (c/s)}} \qquad \ldots (25.38)$$

where Δ is the displacement in frequency between the sample resonance and the Me_4Si resonance. On this scale, τ is positive for all but very acidic protons. This scale is most widely used for work with protons and is measured in parts per million (ppm).

Experimental Arrangement

The experimental method for the determination of nuclear magnetic resonance was developed independently by F.M. Purcell and Bloch in 1946. A simplified diagram of a nuclear magnetic resonance spectrometer is shown in Fig. 25.11. A magnetic field H varying from 0 to 10.000 gauss is applied and this field produces an equidistant splitting of the nuclear energy levels. Transitions between the energy levels are stimulated by radiation from the radio frequency transmitter which sends out electromagnetic radiation from the transmitter coil. The sample will absorb the radiation if the frequency of the oscillating field satisfies equation (25.31). The transitions are detected in the indicator. Usually, a cathode ray oscillograph is used as indicator.

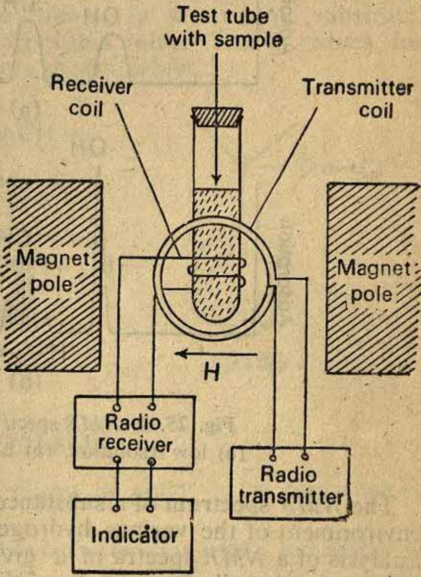


Fig. 25.11. Schematic representation of an *NMR* spectrometer.

The resonance condition is achieved by superimposing a small variable magnetic field. The *NMR* spectra of ethyl alcohol is shown in Fig. 25.12. The low resolution (Fig. 25.12*a*) shows three absorption peaks in an area ratio 1 : 2 : 3, corresponding to $-OH$, $-CH_2$ and $-CH_3$ respectively. Each of these peaks also has a fine structure as shown in Fig. 25.12(*b*). The three peaks arise because different protons in the molecule have slightly different magnetic environments. As a result of this, hydrogen atom interacts differently with the applied magnetic field. Further the electrons surrounding a nucleus are acted upon by the external field to produce an induced diamagnetism which shields the nucleus.

The shielding effect is very useful in the determination of molecular structure. It is expressed in terms of chemical shift δ defined as,

$$\delta = \frac{H_{sample} - H_{reference}}{H_{reference}} \times 10^6$$

where $H_{(sample)}$ and $H_{(reference)}$ are the field strengths at which the sample and the reference substance, respectively, are in resonance for a given frequency ν. The chemical shift is measured in parts per million (ppm.). The reference substance which is commonly employed is tetra methyl silane (TMS).

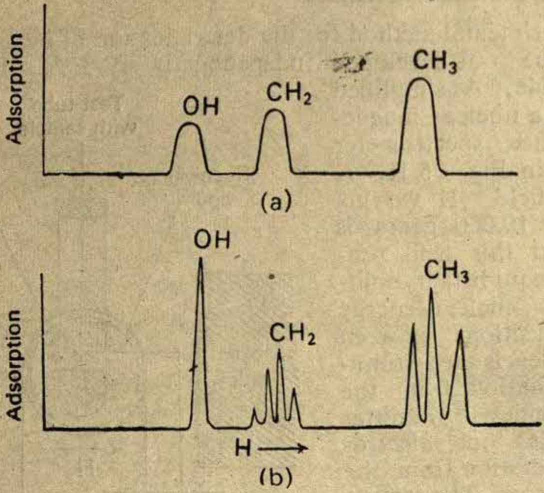


Fig. 25.12. *NMR* spectra of ethyl alcohol.
(*a*) low resolution; (*b*) high resolution

The *NMR* spectrum of a substance is a portrayal of the chemical environment of the various hydrogen atoms of the material. An analysis of a *NMR* spectra of a given compound provides a means of investigating the finer details of the structure of the molecules.

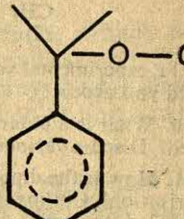
25.10. ELECTRON SPIN RESONANCE SPECTROSCOPY (E.S.R.)

We have seen in the last section that the hydrogen ^{1}H nucleus has spin and therefore a magnetic moment. The electron with its spin, is paramagnetic and also possesses a magnetic moment. Like the proton, the electron will also precess in an applied magnetic field with a precise precessional frequency and will undergo transitions between spin states (spin orientations) if energy of the correct frequency is applied. In ESR we measure the electron spin transitions. The magnetic moment of an unpaired electron is about 700 times that of the proton, so that the sensitivity of e.s.r. detection is much higher than in n.m.r. The e.s.r. spectra can be recorded for radical concentrations as low as 10^{-4} mol dm^{-3}, irrespective of the number of non-radical species present. The e.s.r. can only detect species having unpaired electron spin, for example organic free radicals. In e.s.r. the position of the resonance signal has to be specified as a function of both field strength and frequency; just as in n.m.r. The resonance positions are expressed as a *g* value. The energy of the e.s.r. transitions is given by

$$E=h\nu=gB_0\frac{eh}{4\pi m_e c} \quad \ldots (25.39)$$

where B_0 is the external magnetic field, m_e is the electron mass, e is the electronic charge and c the speed of light; g is a proportionality constant and has the value 2.002319 for an unbound electron. When an unpaired electron is present in an organic substrate, magnetic interaction will shift g from this value. The g values for some common organic radicals are shown below.

CH_3—	CH_2=CH—
2.00255	2.00220
C_2H_5—	CH_2=CH−CH_2—
2.00260	2.00254



2.0155

PROBLEMS

1. Explain the term parachor and discuss its utility in the elucidation of structure of molecules.

2. The refractive index n^{20}_{D} of carbon tetrachloride is 1.4573, the density at 20°C, is 1.595g cm^{-3} and the molecular weight is 153.84. Calculate the molar refraction.

Ans. 26.51 cm^3 mol^{-1}

3. In the ground state of the $^1H^{35}Cl$ molecule, the equilibrium internuclear distance R_0 is 1.2746 Å. What is the position of the centre of gravity?

Ans. On the HCl axis, 0.0354 Å away from the Cl nucleus.

4. Calculate the rotational constant B for HB, molecule where the internuclear distance is 1.2325Å.

Ans. $^1H^{11}B$, rotational constant $B=12.02$ cm^{-1}.

5. Calculate the parachor value for C_2H_6, given that the parachor values for CH_3Cl, CH_4 and HCl are 110, 73 and 71 respectively.

Ans. 112

6. The molar refractions for CH_3I, CH_3Br, HBr and CH_4 are 19.5, 14.5, 9.9 and 6.8 respectively. Calculate the molar refraction value for CH_2BrI.

Ans. 27.2.

7. Arrange in order of decreasing dipolemoment (group together compounds having the same value)—Cl_2, SO_2, CO_2, H_2O, O-dinitrobenzene, HI and CH_4.

Ans. O-dinitrobenzene, H_2O, HI (Cl_3, CO_2, CH_4).

8. Calculate the maximum number of vibrational degrees of freedom for

(*a*) hydrogen fluoride,

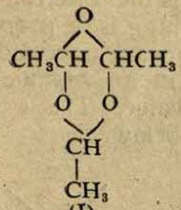
(*b*) hydrogen cyanide,

(*c*) hydrogen sulphide,

(*d*) carbon tetrachloride.

Ans. (*a*) 1, (*b*) 4, (*c*) 3, (*d*) 9.

9. Acetaldyhyde forms a liquid polymer known as paraldehyde $(C_2H_4O)_3$ on polymerization. Two structures have been proposed for the compound:



(I)

$CH_3CH(OH)CH_2CH(OH)CH_2CHO$

(II)

The experimental value of parachor for paraldehyde is 298.7. Which structure would you accept?

10. What is a polar molecule? How is the permanent dipole moment determined? Discuss various applications of dipole moments.

11. How is the dipole moment of a polar molecule determined from the molar polarisation? Outline the application of dipolemoment to the determination of molecular structure.

12. What do you understand by (*i*) line spectra and (*ii*) band spectra? Describe the method used for the study of spectra of elements.

13. What information can be drawn regarding the structure of a molecule from study of its Rotational Spectra?

14. Write short notes on

(*a*) Molecular volume,

(*b*) Raman Spectra,

(*c*) Molar Refraction.

15. Calculate the dipole moments of ortho- meta- and para-chlorotoluene. The dipole moment of toluene is 0.37 D and of chlorobenzene 1.58 D.

16. Differentiate between paramagnetic and diamagnetic substances.

17. What is meant by Nuclear Magnetic Resonance. Describe a method for determining the nuclear magnetic resonance spectra of a molecule.

18. Sketch the expected nuclear magnetic resonance spectra for the protons in *n*-propyl, isopropyl, and tert-butyl alcohols. Indicate clearly the number of components in each band.

19. What do you understand by the term, Polarization of molecules? Differentiate clearly between the terms: induced polarization and orientation polarization.

20. Explain with examples, the usefulness of physical methods in the study of molecular structure.

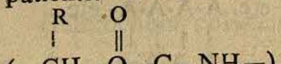
Chapter 26

POLYMERS

26.1 INTRODUCTION

Polymers are one of the most important products, which find an important place in every walk of modern civilisation. The term *polymer* (Greek word: poly+meros, means, many parts) denotes a molecule produced by the repetition of some simpler unit, called the mer or the monomer.

The term *macromolecule* (big molecule) is also often used to cover the large molecules of complex structure. A naturally occurring macromolecule is insulin, a protein hormone, which occurs in the pancreas, and is best known agent to lower blood sugar in diabetic patients. It has the repeating units with amide linkages, *i.e.*



$(-\overset{\overset{\displaystyle R}{|}}{C}H-\overset{\overset{\displaystyle O}{\|}}{O}-C-NH-)_n$, where $n=51$ and *R* has sixteen variations. The science of macromolecules is divided between biological and non-biological materials, each having vital importance in our daily life. Biological polymers, *i.e.*, proteins, nucleic acids (DNA, RNA), starch, cellulose and enzymes are complex macro molecules form the very foundation of life and intelligence, and provide much of the food for the existence of man. This chapter however, is concerned mainly with the chemistry of some polymers. These are primarily the synthetic materials used for plastics, fibres, and elastomers, and a few naturally occurring polymers, such as rubber, wool, and cellulose. The polymers are truly indispensable to mankind, as they are used to meet the basic needs—clothing, shelter, communication, and transportation, as well as to the conveniences of modern living.

The name of a polymer is usually derived from the name of the monomer (repeat unit) by prefixing the word poly to it. To illustrate the polymerization product of ethylene is known as polyethylene and that of sytrene is called polystyrene. The number of repeating units in the chain is called the degree of polymerization (DP), and specifies the length of the chain. Degree of polymerization is denoted by the letter *n* or *P*. The molecular weight of the polymer is the product of the molecular weight of the repeat unit and the degree of polymerization, *i.e.*,

$$\text{M. pol.}=n\times M_u$$

or

$$n \text{ (Degree of polymerization)} = \frac{M_{\text{poly}} \text{ (mol. wt. of polymer)}}{M_u \text{ (mol. wt. of repeat unit)}}$$

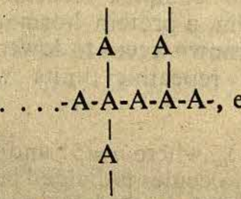
The degree of polymerization may vary over a wide range, *i.e.*, from a few units to 10,000 and even more. Polymers with high *DP* are called high polymers and are mostly useful for plastics, rubbers, or fibres etc., while those with low *DP* are known as oligomers.

26.2. CLASSIFICATION OF POLYMERS

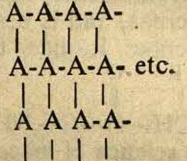
A polymer may consist of monomers of identical or of different chemical structure If it has identical units then it is known as homopolymer, whereas a polymer containing several types of monomeric units in its chain is known as copolymer, or mixed polymer. In some cases the repetition is linear and a chain is built up from its links. However, in cases the chains are branched or interconnected, to form the dimensional structures

. .-A-A-A-A- . . ., etc.

Linear polymer



Branched polymer



Three-dimensional polymer (cross-linked)

Co-polymers may also be linear, branched or three-dimensional. The monomer residues, in co-polymer molecules may be arranged in the chain regularly or at random, according to the law of chance. Copolymers of the former group are called regular-copolymers and those of latter type, statistical or irregular-copolymers.

Co-polymers with long sequence of two monomers can have two arrangements of chains: (*i*) linear copolymer in which the units of each type form fairly long continuous sequences (blocks) is known as block copolymer (see on next page).

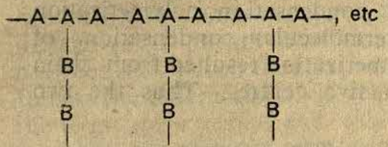
(*ii*) Branched copolymer, with monomer of one kind grafted into a "backbone" of the second monomer type is termed as graft copolymer (see on next page).

According to the structure of main chain, all polymers are classified into homochain and heterochain polymers. Homochain polymers contain the chains composed of atoms of the same elements, *e.g* , carbon, sulphur phosphorus, etc. (see on next page).

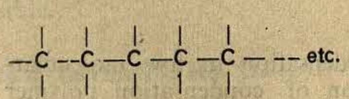
In heterochain polymers the main chain is made up of atoms of different species, *e.g.*,

—A—A—A—A—B—B—B—B—A—A—A—A—B—B etc.

Block polymer

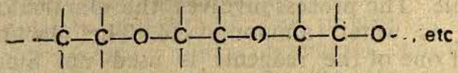


Graft polymer



$-\mathrm{C}-\mathrm{C}-\mathrm{C}-\mathrm{C}-\mathrm{C}-\,-\,-\text{ etc.}$

Carbon-chain polymer



$-\,-\mathrm{C}-\mathrm{C}-\mathrm{O}-\mathrm{C}-\mathrm{C}-\mathrm{O}-\mathrm{C}-\mathrm{C}-\mathrm{O}-\,..\text{ etc}$

Heterochain polymer

On the basis of chemical composition, the polymers can also be classified as:

(*a*) **Organic polymers.** Organic polymers include compounds containing carbon, hydrogen, oxygen. nitrogen, sulphur, and halogen atoms. Oxygen, nitrogen, or sulphur may also be present in the backbone chain.

(*b*) **Elemento-organic (hetero-organic) polymers.** These include the following classes:

(*i*) Compounds containing carbon atoms and hetero atoms (except for nitrogen, sulphur and oxygen atoms) in their chains.

(*ii*) Compounds with inorganic chains if they contain side groups with carbon atoms connected directly to the chain.

(*iii*) Compounds having carbon atoms in the main chain and hetero-atoms (except for nitrogen, sulphur, oxygen and halogen atoms) in side groups connected directly to the carbon atoms of the chain. For example, polysiloxanes, polytitanoxanes etc.

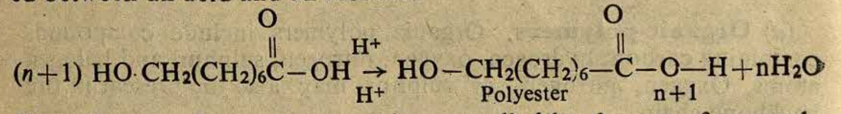
(*c*) **Inorganic polymers.** They include polymers containing no carbon atoms. Their chains are composed of different atoms joined by chemical bonds, while weaker intermolecular forces act between their chains. Polysilanes, polygermanes, polysilicic acid, polyphosphates, polyarsenates, etc. are examples of inorganic polymers.

26.3. POLYMERIZATION PROCESSES

The processes of polymerization were classified by the W.H. Carothers (1929) into two groups, *i.e.*, *Condensation* and *Addition* polymerizations. In 1953, Flory amended, Carother's original distinction between addition and condensation polymerization. He laid special emphasis on the mechanisms by which the two types of polymerization, proceed. It was observed that condensation polymerization was preceded by the stepwise intermolecular condensation of reactive groups and the addition polymerization resulted from chain reactions involving some sort of active centres. Thus the two classes of polymerization are:

(1) Condensation Polymerization

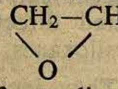
This is entirely analogous to condensation in low molecular-weight compounds. For the formation of condensation polymer there is union between two polyfunctional molecules to produce the large polyfunctional molecule. The process involves the elimination of a small molecule such as water, ammonia etc. The reaction continues until almost all of one of the reagents is used up. Since there is an equilibrium between reactants and products, the rate of conversion can be controlled by the rate of removal of one of the products. A good example is, esterification, where water is eliminated between an acid and an alcohol.



$$(n+1)\ HO\cdot CH_2(CH_2)_6\overset{\overset{O}{\|}}{C}-OH \xrightarrow[H^+]{H^+} \underset{\text{Polyester}}{HO-CH_2(CH_2)_6-\overset{\overset{O}{\|}}{C}-O-H}_{n+1}+nH_2O$$

Here, the rate of conversion can be controlled by the rate of removal of water.

(2) Addition or Chain-reaction Polymerization

This type of polymerization involves chain reactions. The chain carrier in such reactions, may be an ion or a reactive substance with one unpaired electron called a free radical. Chain polymerization is characteristic of compounds with multiple bonds, *e.g.*, ethylene $CH_2=CH_2$, isobutylene $(CH_3)_2=CH_2$, and vinyl chloride $CH_2=CHCl$, or of unstable rings containing hetero-atoms, *e.g.*, ethylene oxide  $\underset{O}{CH_2-CH_2}$. Depending upon the active center, which may be a free radical or an ion, the reaction is one of radical or ionic polymerization, respectively. A free radical is produced by the decomposition of an initiator. The free radical then attacks to open the double bond of a vinyl monomer or ring of a cyclic compound and adds to it, with an electron remaining unpaired. Within a very short span of time (usually a few seconds or less) many more monomers add successively to form a long chain with active centres. Finally, chain termination results from saturation of the macro radical and may occur by the combination of free radicals, disproportionation of chain transfer.

With few exceptions, chain-reaction polymerization results in the formation of homochain polymers, where as step-reaction polymerization produces heterochain polymers. Polymerizations are classified without regard to loss of a small molecule (*e.g.*, polyurethanes are formed by step-reaction polymerization or type of interunit linkage (*e g.*, phenol-formaldehyde resins result from stepwise polymerization even though they lack interunit functional groups). In case the differentiation is required on the basis of mechanism, the terms *step-reaction* and *chain-reaction* are used; but to avoid confusion the common terms *condensation* and *addition* are permissible.

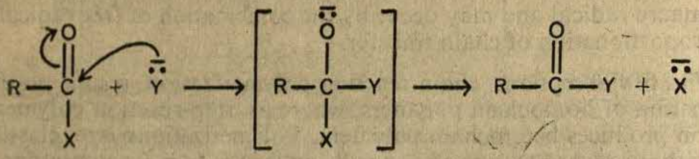
26 4. CHEMISTRY OF POLYMERIZATION

The rections by which complex macromolecules are formed are not completely understood. The process of building up polymers from simple repeating units (monomers) can proceed with many variations. As noted earlier, on the basis of mechanisms the two types of polymers are formed. Condensation polymers are usually formed by the step-wise intermolecular condensation of the reactive groups, addition polymers ordinarily result from chain reactions involving some sort of active centres.* The chemistry of each type is discussed in this section except those which are not yet confirmed in detail.

(*a*) Step-wise Polymerization

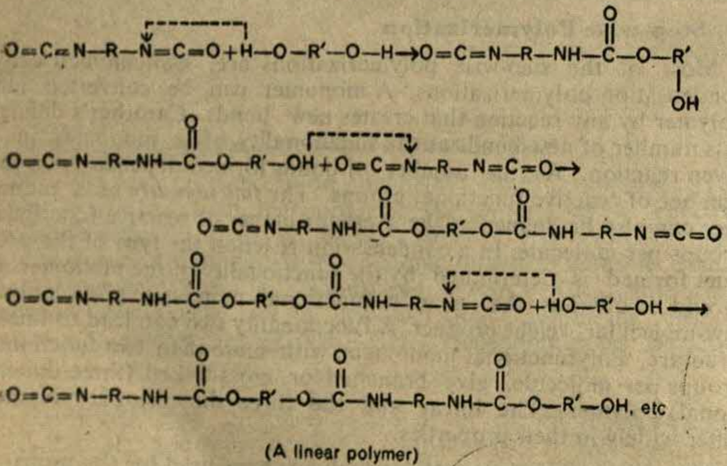
Most of the step-wise polymerizations are, stoichiometrically, condensation polymerizations. A monomer can be converted into polymer by any reaction that creates new bonds. Carother's defined this number of new-bonds as the functionality of a monomer in a given reaction. As the number of bonds formed depends upon the number of reactive functional groups. The *functionality* of a monomer can also be defined as the average number of reactive functional groups per molecule. In a condensation reaction the type of the product formed is determined by the functionality of the monomer. It should be obvious that a monofunctional monomer gives only a low-molecular-weight product. A functionality two can lead to linear structure. Polyfunctional monomers, with more than two functional groups per molecule, give branched or cross-linked (three-dimensional) polymers The linear and the three dimensional polymer differ widely in their properties.

The most important reaction which has been used for the preparation of condensation polymers is that of addition and elimination at the carbonyl double bond of carboxylic acids and their derivasives. The generalized reaction is



where R may be alkyl or aryl group, X may be·OH, OR′, NH_2, NHR, $O-\overset{O}{\overset{\|}{C}}-R$, or Cl; and Y may be $R'O^-$, R′OH, $R'NH_2$ or $R'COO^-$. The meta-stable intermediate can either return to the original state by eliminating Y or proceed to the final state by eliminating X. The formation of polymers, polyamides, nylon—66, poly (ethylene terephathalate), polyurethanes, polyureas, polysulphonamides, polyphenyl esters, etc. provides some typical examples of this reaction.

In simple terms, it can be stated that stepwise polymerization, is the combination of several molecules by stepwise addition of monomer molecules to one another as a result af migration of some mobile atom, usually a hydrogen atom, from one molecule to another. To illustrate the formation of polyurethanes from di-isocyanates and dihydric alcohols:



(A linear polymer)

A trihydric alcohol will give a cross linked polymer.

(*b*) **Chain Polymerization**

Chain polymerization is characteristic of unsaturated monomers. Ethenic polymerization is an economically important class whose kinetics typify chain polymerization. The terms 'vinyl', 'olefin', or 'addition' polymerization are often used, although they are more restrictive. Flory showed conclusively that chain polymerization proceeds by and requires the steps of initeraction, propagation, and termination typical of chain reactions in low-molecular-weight species. The three stages which are essential to the formation of a useful high polymer can be represented as:

(*i*) **Initiation**. This involves the creation of an 'active' centre, and can also be termed as activation of the monomer molecule, *i.e.*,

$$M \rightarrow M^*$$

(Excited monomer molecule)
or
active centre

(*ii*) **Propagation**. Propagation is the addition of more monomer to chain end-usually very rapid (mol. wt. 10^7 in one-tenth of a second) to final molecular weight. This is shown below:

$$M^* + M \rightarrow M_1^*$$
$$M_1^* + M \rightarrow M_2^*$$
$$M_2^* + M \rightarrow M_3^*$$

....
....
....

$M^*_{n-1} + M \rightarrow M_n^*$ (Activated growing polymer molecule)

(*iii*) **Termination**. In this step there is disappearance of the 'active' centre

$M_n^* \rightarrow M_n$ (unactivated polymer molecule)

The active centre in chain polymerization reactions may be a free radical or an ion, and the reaction is one of radical or ionic polymerization, respectively.

(*c*) **Radical Polymerization**

The intermediates having an odd number of electrons (an unpaired electron) are known as free radicals. They can be generated in a number of ways, including thermal decomposition of peroxides on hydroperoxides; photolytic decomposition of covalently bonded compounds; dissociation of covalent bonds by high-energy radiation ($\alpha-$, $\beta-$, or γ-rays); oxidation reduction reactions; and electrochemical interaction. The stability of the free radicals varies widely. Tertiary radicals are more stable and less reactive than secondary radicals, which are in turn more stable and less reactive than the primary ones. The benzyl radical is less reactive than phenyl radical, the allyl is quite stable and is quite unreactive.

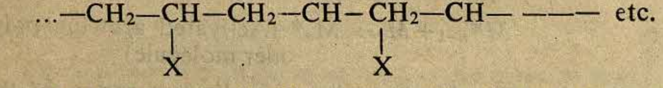
(*i*) **Initiation**. Once the primary free radicals (free radicals produced in the first stage) are produced by physical or chemical effects in the presence of a vinyl monomer ($CH_2{=}CHX$), the radical adds to the ethylenic double bond of an unexcited monomer molecule with the regeneration of another radical. If the radical formed by decomposition of the initiator I is designated $\dot{R}$,

$$I \xrightarrow{\text{decomposition}} 2\dot{R} \quad \text{(Primary free radical)}$$

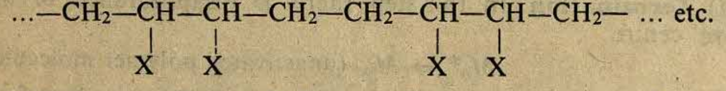
$$CH_2{=}CHX + \dot{R} \longrightarrow RCH_2\dot{C}H{-}X \quad \text{(Chain radical)}$$

The regeneration of the new free radical is characteristic of chain reactions as this is capable of further interaction with the initial monomers. The efficiency with which radicals initiate can be estimated by comparing the amount of initiator decomposed with the number of polymer chains formed. Most initiator in vinyl polymerizations have 60-100% efficiency. The low efficiency is mainly due to the recombination of the radical pairs before they move apart, this is known as *cage-effect*.

(*ii*) **Propagation**. The chain radical formed in the initiation step is capable of adding sucessive monomers to from macroradicals. The chain propagation reaction determines the rate of the polymerization, the molecular mass of polymer, the structure of the polymer chain, *i.e.*, the mode of monomer addition ('head-to-head' or head-to-tail)*, the degree of branching etc.



$$\ldots{-}CH_2{-}\underset{X}{\underset{|}{CH}}{-}CH_2{-}CH{-}CH_2{-}\underset{X}{\underset{|}{CH}}{-}\;{-}{-}{-}\;\text{etc.} \qquad \text{(I)}$$



$$\ldots{-}CH_2{-}\underset{X}{\underset{|}{CH}}{-}\underset{X}{\underset{|}{CH}}{-}CH_2{-}CH_2{-}\underset{X}{\underset{|}{CH}}{-}\underset{X}{\underset{|}{CH}}{-}CH_2{-}\ldots\;\text{etc.} \qquad \text{(II)}$$

Addition according to the former scheme is called head-to-tail', configuration in which the substituents occur on alternate carbon, atoms, and that according to the latter scheme 'head-to-head' or 'tail-to-tail'. In most polymerizations, monomers combine according to most favoured (steric factors) head-to-tail scheme).

The propagation step is given by the following reaction:

$$R(CH_2{-}CHX)_n\, CH_2{-}\dot{C}H{-}X + CH_2 + CHX$$

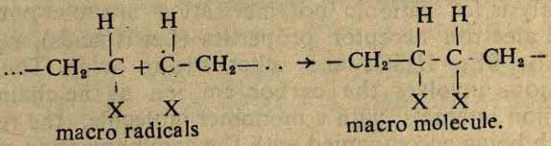
$$\underset{\text{macro radical}}{R(CH_2{-}CHX)_{n+1}CH_2{-}\dot{C}HX}$$

---

*(In a polymerization process repeating units may combine according to scheme I or scheme II:)

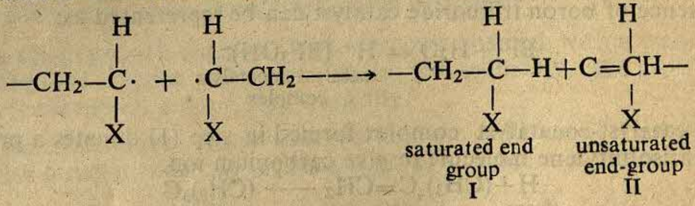
(*iii*) **Termination**. Propagation would continue until the supply of monomer is exhaused. The radicals also have the strong tendency to react in pairs to form a paired-election covalent bond causing thereby loss of activity. In free radical polymerization, this tendency is compensated by the small concentration of radical species compared to monomers. Chain termination results from saturation (deactivation) of the macroradical and may occur in two ways:

(1) *Combination or coupling*. Combination consists in the neutral saturation of two macroradicals or of a macroradical and a low-molecular free radical:



$$\ldots-CH_2-\overset{H}{\underset{X}{C}}\cdot + \cdot\overset{H}{\underset{X}{C}}-CH_2-\ldots \rightarrow -CH_2-\overset{H}{\underset{X}{C}}-\overset{H}{\underset{X}{C}}-CH_2-$$

(2) **Disproportionation**. This involves the transfer of a hydrogen atom from one macroradical to another to form two macromolecules with one saturated and one unsaturated end group.



$$-CH_2-\overset{H}{\underset{X}{C}}\cdot + \cdot\overset{H}{\underset{X}{C}}-CH_2 \longrightarrow -CH_2-\overset{H}{\underset{X}{C}}-H + \overset{H}{C}=\underset{X}{C}H-$$

Chemical substances capable of reacting with free radicals to terminate the reaction chain are called polymerization *inhibitors*, for example—hydroquinone and trinitrobenzene. Chemical compounds which are only chain transfer agents and do not affect the rate of polymerization but determine the molecular mass or polymer, are termed as polymerization regulators, or modifiers.

(*d*) Ionic Polymerization

Chain reaction polymerization can occur by several mechanisms other than those involving free radicals as discussed earlier. The most important among these, are the reactions in which the chain carriers are carbonium ions (cationic polymerization) or carbanions (anionic polymerization). Ionic polymerization proceeds in the presence of catalysts and is also called catalytic polymerisation. The reactivity of the ethenic monomers to polymerization by radicals, ions and complexing agents varies with the structure in a manner which can be correlated though not always quantitatively predicted. It can be seen that, for the vinyl monomer ($CH_2=CH-X$), cationic initiation is favoured when X is electron-releasing and anionic when X is electron-withdrawing. This is because monomers with electron releasing groups attached to the double-bonded carbons are capable of forming stable carbonium ions, where as monomers with electron-with-drawing substituents form stable carbanions. Ionic polymerizations tend to be very rapid even at low temperatures. The polymerization of isobutylene with $AlCl_3$ or BF_3 is carried out commercially at —100°C and an estimate of the life-time of a growing chain of isobutylene in this case is about 10^{-6} sec., much shorter than the usual life time of a free-radical chain.

(1) **Cationic, or carbonium polymerization**. This involves the formation of a carbonium ion which is a polar compound with tricovalent carbon atom carrying a positive charge, $R-\overset{+}{C}H-R$. Typical catalysts for cationic polymerization are compounds with pronounced alectron acceptor properties (Lewis acids), *e.g.*, $AlCl_3$, $AlBr_3$, $SnCl_4$, BF_3, H_2SO_4 and other strong acids. The cationic polymerization, involves the carbonium ion as the chain carrier. Carbonium ion interacts with a monomer molecule, the reaction of chain growth being accompanied with the communication of positive charge along the chain. Consequently, the growing chain itself is a cation with a molecular mass increasing in the course of polymerization. For example, the polymerization of isobutylene in the presence of boron trifluoride catalyst can be represented as:

$$BF_3+H_2O \rightleftharpoons \underset{\substack{\text{catalyst-cocatalyst}\\ \text{complex}}}{H^+\,(BF_3OH)^-} \qquad (1)$$

The catalyst-cocatalyst complex formed in step (1) donates a proton to an isobutylene molecule to give carbonium ion.

$$\underset{\substack{\text{(from}\\ \text{complex)}}}{H}+(CH_3)_2C=CH_2 \longrightarrow \underset{\substack{\text{carbonium}\\ \text{ion}}}{(CH_3)_3C}$$

(2) **Anionic, or carbanion polymerization**. Anionic polymerization involves the formation of a carbanion, a compound with a trivalent carbon atom carrying a negative charge.

$$(CH_3)_3\overset{+}{C}+(CH_3)C=CH_2 \longrightarrow (CH_3)_3C-CH_2-\overset{+}{C}(CH_3)_2$$

$$(CH_3)_3C-CH_2-C^+(CH_3)_2+(CH_3)_2C=CH_2 \longrightarrow$$
$$(CH_3)_3-C-CH_2C(CH_3)_2-CH_2-C^+(CH_3)_2$$

Thus there is reformation of a carbonium ion at the end of each step by the 'head-to-tail' addition of monomer to ion.

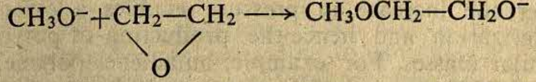
Chain termination apparently occurs as a result of the mutual collision of the ends of growing ion to yield a polymer molecule with terminal unsaturation and the original complex,

$$CH_3[(CH_3)_2C(CH_2)]X\ C(CH_3)_2{}^+(BF_3OH)^-$$
$$\downarrow$$
$$\underset{\text{Polymer}}{CH_3[(CH_3)_2C(CH_2)]X}\ \underset{\text{Catalyst-cocatalyst complex}}{C(CH_3)=CH_2+H^+(BF_3OH)^-}$$

The third component present in low concentration which usually has pronounced effects on polymerization is called cocatalyst. The efficiency of the catalyst is dependent on the acid strength of the catalyst-co-catalyst complex. In cationic polymerization, the catalyst is not in the macromolecule.

(3) **Anionic, or carbanion polymerization**. Anionic polymerization involves the formation of a carbanion, a compound with a trivalent carbon atom carrying a negative charge. Catalyst for carbanion polymerization include, alkali metals, alkali metal amides, alkoxides, alkyls, aryls, hydroxides, and cyanides. They are electron releasing groups. Polymerization occur by the carbanion mechanism in the case of monomers containing electronegative substituents at one of the carbon atoms connected by a double bond. The initiation of ionic chains involves the addition of a negative ion to the monomers, with the opening of a ring or bond and growth at one end:

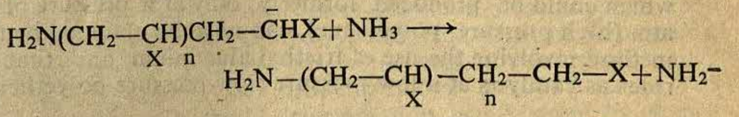
$$NH_2^- + CH_2{=}CHX \longrightarrow H_2N{-}CH_2CHX^-$$



The more basic the ion (anion), the better it serves to initiate chains. Thus $C_6H_5CH_2^-$ is powerful initiator than NH_2^- which is stronger than OH^- in the anionic polymerization of styrene.

The chain growth reaction is always accompanied with a transfer of a negative charge along the chain, consequently, the growing chain is always an anion of growing size.

Chain termination occurs as a result of the collision of a growing ion with a molecule of the medium such as an ammonia molecule:



$$H_2N(CH_2{-}\underset{X}{CH})_nCH_2{-}\bar{C}HX + NH_3 \longrightarrow H_2N{-}(CH_2{-}\underset{X}{CH})_n{-}CH_2{-}CH_2{-}X + NH_2^-$$

Thus energy growing chain contains the $-NH_2$ group. The termination step is always unimolecular and usually by transfer.

In anionic polymerization, the end group of a growing molecule possesses high activity and great stability. Hence the polymers obtained by anionic polymerization method retain active centres at the end of the chain, which are capable of initiating the polymerization of monomers. Such polymers are called living polymers. The polymer can be 'killed' by addition of a terminating agent, like water at the end of the reaction. Anionic polymerization has great advantages, since spontaneous chain termination does not occur.

26 5. EFFECTS OF VARIOUS FACTORS ON POLYMERIZATION RATE EFFECT OF TEMPERATURE

The rate of radical polymerization reaction usually increases with rising temperature. The variation in temperature also effects the structure of the resulting products. To illustrate—the rise in temperature during the polymerization of butadiene causes ring dimer to form instead of chain molecules. That is why butadiene is always polymerized below 60°C. The size and structure of the polymer chain depend upon the temperature. It has been established that low temperature favours formation of higher molecular mass polymer in most of the cases.

Raising the temperature increases the degree of branching of polymer.

Effect of Pressure

Pressure changes have also marked effect on the rate of polymerization. If pressure is increased this would result in increase in the number of collisions between the active centres and the monomers. Hence, the rate of polymerization will considerably be increased. Further, the increase in pressure enables a lower temperature of polymerization and hence the production of polymers with higher molecular masses. For example, butadiene polymerization takes 45 hours at 7000 atm and 48°C, and only 19 hours at the same pressure and 61°C, but at 1 atm it takes hundred of days.

Effect of Catalyst

Catalyst plays a vital role in the chain polymerization. Ionic polymerizations always require a catalyst. In the presence of catalyst, the polymerization can be affected at low pressure. The use of elevated pressure for polymerization should always be considered in conjunction with the choice of a catalyst. To illustrate polyethane, which could be produced formerly only at a pressure of 1000-2000 atm (high pressure polyethene), can now be obtained by the Ziegler method involving the use of triethyl aluminium and titanium chlorides as catalysts at a low pressure (low-pressure polyethene).

26.6. MOLECULAR WEIGHTS OF POLYMERS

Since polymerisation reactions, both synthetic and natural, can lead to high molecular weight compounds. The reaction chain is however broken by some termination process that usually, occurs in a random manner with respect to the size, to which the polymer, has already grown. It follows, therefore, that polymers possess a range of molecular weights and that any data for the size or weight of the molecules of a polymer must represent some sort of average value. The molecular weights of polymers lend themselves to two types of averages, *i.e.*, (*i*) number average molecular weights and (*ii*) weight average molecular weights.

Number average molecular weight. It is defined as the weight of the sample divided by the total number of moles n in the sample, *i.e.*,

$$Mn = \frac{\text{weight}}{n}$$

If a method of molecular weight determination leads to the number of particles, or molecules, that are present, in a given weight of a sample, will give the number average molecular weight. Let us consider a polymer as made up of fractions consisting of n_1 moles of molecular weight M_1', n_2 moles of molecular weight M_2 and so on, then M_n the number average molecular weight is given by the expression:

$$M_n = \frac{n_1M_1 + n_2M_2 + \ldots\ldots}{n_1 + n_2 + \ldots\ldots} \qquad \ldots (26.1)$$

$$= \frac{\sum_i n_iM_i}{\sum_i n_i}. \qquad \ldots (26.2)$$

On the other hand if in an experiment each particle makes a contribution to the measured result according to its molecular weight, we get *weight average molecular weight* of the polymer, M_w which is defined as,

$$M_w = \frac{\sum_i n_iM_i^2}{\sum_i n_iM_i}. \qquad \ldots (26.3)$$

Molecular weight of a polymer can be determined by relative or absolute methods. Many properties of polymers which depend upon molecular weight, such as—solubility, elasticity, adsorption on solids, and their tear strength, can be corrected with an average molecular weight. Once correlated, the property can be used as a measure of molecular weight. The weight determination can be done by chemical or physical methods of functional group analysis, by measurement of the colligative properties, light scattering, or ultra-centrifugation, or by measurement of dilute solution viscosity. In all these methods, except the last, molecular weights can be calculated without reference to calibration by another method and, therefore, are absolute methods. Dilute solution viscosity is not a direct measure of molecular weight. All molecular weight methods, except a few end group analysis methods, require solubility of the polymer, and all involve extrapolation to infinite dilution or operation in a solvent in which ideal solution behaviour is attained. Some important methods used in practice for determining the molecular weight and size of macromolecules in dilute solutions are discussed below.

26.7. METHODS OF DETERMINING MOLECULAR WEIGHT

Some of the important methods employed for the determination of molecular weights of polymers are :

(1) Osmometry

Osmometry can be used for determining molecular masses from 10^4 to 10^6. This is one of the most accurate methods, though due to its lengthy and tedious experimental procedure it cannot be frequently used for fast molecular weight determination. The method, involves the measurement of the osmotic pressure of solutions at several concentrations. The instrument used for the determination of molecular-weights by this method is called *osmometer*. In an osmometer, the solvent is separated from the solution by a semipermeable membrane. It then passes through the latter into the solution, until the level of the solution in the capillary stops rising. The osmotic pressure, at this stage, is equal to the weight of the hydrostatic column of the solution.

The capillary forces also raise the liquid in the capillary to some extent, to account for these forces a capillary having radius equal to that of osmometer capillary, is immersed in the liquid. This capillary is known as control capillary. The difference in the level of osmometer capillary and control capillary is the measure of osmotic pressure. The two more commonly used methods are:

(*a*) **Static method**. This method involves the measurement of the equilibrium difference of levels in the osmometer. The osmometer for this method are very simple in design, but equilibrium in such an osmometer is reached after a long time. The concentration of the solution near the membrane may increase as a result of absorption of polymer, at equilibrium. This shortcoming can be eliminated by proper production and storage of membranes. For cross linking polymers this method is usually not recommended.

(*b*) **Dynamic method**. This method consists of measuring the rate of penetration of solvent through the membrane, depending upon the pressure applied. The main advantage of this method is that the measurements take very less time as compared to the static method.

Choice of membrane. A choice of suitable membrane plays an inportant role in osmometric measurements. The membrane should be permeable to the solvent and impermeable to the polymeric solute. It should satisfy the following two conditions:

(*a*) The membrane should not swell to any great extent in the solvent.

(*b*) It should have sufficiently fine pores to allow the solvent molecules to pass through freely.

These days membranes are prepared from cellophane and specially treated films of denitrated cellulose nitrate. The untreated cellophane membranes have small pore radius and subsequently take long time to reach equilibrium. To increase the pore size, the cellophane is treated with ammonia solution or other reagents. For this reason only cellophane is generally used for measuring molecular weights of very low-molecular polymers. Denitrated cellulose nitrate membranes give better and much more satisfactory results.

The polymer is first throughly freed from impurities by reprecipitation before determining the molecular-weight. A stock solution, usually 1 per cent is prepared from a purified polymer. From the stock solution, working solutions of various concentrations, varying from 0.075 per cent to 0.5 per cent are prepared by dilution. One fifth of the one per cent solution is left undiluted for exact determination of its concentration. In order to measure the osmotic pressure, a polymer solution and pure solvent are placed on the opposite sides of a semipermeable membrane. The membrane is so selected as to permit only solvent and not the polymer. To establish equilibrium, the pressure on the solution side must be greater. The osmotic pressure, can be measured at several concentrations either by waiting for equilibrium or by measuring and compensating for pressures automatically.

To calculate molecular weight of a polymer the osmotic pressure values obtained for the different solutions are divided by the corresponding concentrations and the resulting reduced osmotic pressures are plotted in π/C_n versus C. The straight line obtained in this way is extrapolated to zero concentration as shown in Fig. 26.1. The resulting values A (intercept with the ordinate axis) is substituted in the equation given below and molecular weight is calculated.

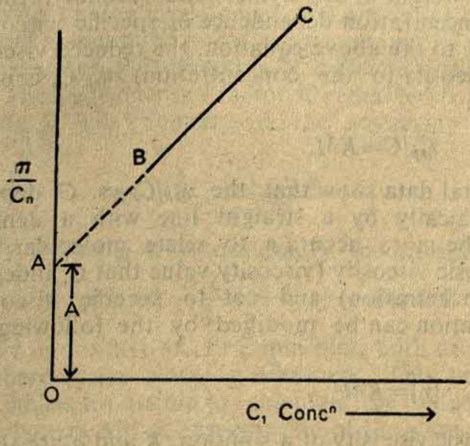


FIG. 26.1. Variation of reduced osmotic pressure with concentration.

$$\left(\frac{\pi}{C_n}\right)_{C_n \to O} = \frac{RT}{M} \qquad \ldots (26.4)$$

or

$$M=\frac{RT}{\left(\frac{\pi}{C_n}\right)_{C_n\to O}} \quad \ldots (26.5)$$

where, π=osmotic pressure (g/cm^{-2})=$h\rho$
h=difference in liquid levels at equilibrium, cm.
ρ=density of solvent, g/cm^3.
C=concentration, g/cm^3.
T=absolute temperature, °K.
M=molecular-weight, g/mole.
R=gas constant, 8.48×10^4 g-cm/(mole)(°K).

(2) Viscometry

The first person to draw attention to the usefulness of solution viscosity as a measure of polymer molecular weight was Staudinger, who established the following relationship:

$$\eta_{sp}=KMC \quad \ldots (26.6)$$

where, η_{sp}=specific viscosity of polymer solution,
K=constant,
M=molecular weight of a dissolved polymer.
C=concentration of a polymer in solution.

However, the above relation suffers with two serious drawbacks, first, the coefficient K does not give a constant value, but it depends on the molecular weight of a polymer and secondly, the equation represents the concentration dependence of specific viscosity incorrectly. According to the above equation, the reduced viscosity (ratio of the specific viscosity to the concentration). η_{sp}/C, is independent of concentration.

$$\eta_{sp}/C=KM. \quad \ldots (26.7)$$

But experimental data show that the η_{sp}/C vs. C dependence is represented graphically by a straight line with a definite slope. Hence, it would be more accurate to relate molecular weight of a polymer to intrinsic viscosity (viscosity value that is independent of the solution concentration) and not to specific viscosity. Thus Staudinger's equation can be modified by the following empirical relation,

$$[\eta]=KM^a \quad \ldots (26.8)$$

where, $[\eta]$=intrinsic viscosity of a solution, K and a are the constants characterizing the given polymer-solvent system.

Intrinsic viscosity is determined from the relative viscosity of the dissolved polymer solutions. Then the specific and reduced viscosities are calculated and a plot of η_{sp}/C vs. C is made. The extrapolation of this line to zero concentration, gives the value of $[\eta]$. K and

a are calculated by plotting log $[\eta]$ vs. log M, which represents a straight line having slope, a, and intercept log K.

$$\log [\eta]=\log K+a \log M. \qquad \ldots (26.9)$$

Hencc, K and a, can be determined graphically. Using the same solvent for which K and a, are determined, the viscosities can be calculated.

Owing to the simplicity of the equipment used (viscometer), this method can be very conveniently used in the laboratory.

(3) Light Scattering

Light scattering accounts for many natural phenomena including the colours of the sky, the rainbow, and of most white materials. A media may be transparent or turbid. The turbidity of a medium is due to scattering of light. The scattering of light occurs whenever a beam of light encounters matter. Similarly, when a polymer is dissolved in a solvent, the light scattered by the polymer far exceeds that scattered by the solvent, and is an absolute measure of molecular weight.

Debye gave a solution for the factor of internal interference $P(\theta)$ for the scattering particles of different shape. The Debye relationship is:

$$\frac{H'C}{K}=\frac{1}{MP(\theta)}+2A_2C \qquad \ldots (26.10)$$

where H' is a lumped constant including geometric factors and also the change in refractive index with polymer concentration for the particular system being investigated. θ is the angle at which the intensity of light is measured and C is the concentration. A_2, second virial coefficient and $P(\theta)$ (function of molecular shape) are derived from data. The light intensity factor K is derived from the galvanometer reading I_g. The geometry and the scattering by solvent I_{gs} is compensated by

$$K=\frac{(I_g-I_{gs}) \sin \theta}{1+\cos^2\theta} \qquad \ldots (26.11)$$

since at $\theta=0$, $P(\theta)=1$, it is customary to extrapolate to $\nu=0$ as well as $C=0$. A plot of $\frac{H'C}{K}$ *vs* C at coustant θ and $\frac{1}{MP(\theta)}$ vs. $\sin^2 (\theta/2)$ give intercept $1/M$. In Zimm plot, both can be done simultaneously where a net work is obtained. This method is more precise and makes it possible to calculate the values of molecular masses of polymers without assumption of the shape of macromolecules in a solution.

The presence of dust particles or gelled polymer particles cause a major practical problem in light scattering. A small concentration of these, obscures the scattering by ordinary polymer particles and result in $M_w^{-}=\infty$. The removal of dust can be done by ultra centrifugation.

Appendix I

SI UNITS

The abbreviation SI stands for Systeme International d'Unites, which is a system based on the metric system and approved by the international authority of units (CGPM).

Temperature

The kelvin is used to denote both the temperature on the thermodynamic scale and also a temperature interval. The value of the kelvin is fixed as the temperature of the triple point of water as 273.16 K. The degree clesius (°C) is not an SI unit but is used for many temperature measurements.

The Mole

The mole is defined as the amount of substance that contains the same number of elementary units as there are atoms in 0.012 kg of carbon-12.

The table given below gives the names and symbols for the basic SI units.

Physical quantity	*Name of SI unit*	*Symbol of SI unit*
Mass	kilogram	kg
Length	metre	m
Time	second	s
Thermodynamic Temperature	kelvin	K
Amount of substance	mole	mole
Electric current	ampere	A
Luminous intensity	candela	cd

Derived SI Units

The SI units for physical quantities other than the basic ones are derived by suitable combination of the basic units. For example, the

SI unit of volume is cubic metre (m^3). The litre is not an SI unit, but has been redefined as being equal to a cubic decimetre ($dm^3 = 10^{-3} m^3$). The SI unit of pressure is newtons per square metre (Nm^{-2}). The atmosphere or millimetres of mercury are related to SI units as follows:

$$1 \text{ atm} = 760 \text{ mm Hg} = 101,\ 325 \text{ Nm}^{-2}$$

The present trend is to use the SI units, but in this book we have employed both the metric and SI units.

Appendix II

SI VALUES OF SOME FUNDAMENTAL CONTENTS

Quantity	*Symbol*	*Value*
Gas Constant	R	8.3143 JK^{-1} mol^{-1}
Avagadro's Number	N	6.0222×10^{23} mol^{-1}
Ice-point temperature	T_{ice}	273.150 K
Boltzmann constant	k	$1.3806 \times 10^{-23} JK^{-1}$
Molar volume of an ideal gas at NTP	$\frac{RT_{ice}}{101325\ P_a}$	0.022414 m^3 mol^{-1}
Faraday constant	F	$9.6487 \times 10^4 C$ mol^{-1}
Velocity of light	C	2.99793×10^8 ms^{-1}
Planck constant	h	6.6262×10^{-34} Js
Atomic mass constant	m_u	1.66053×10^{-27} kg
Bohr magneton	μ_B	$9.2741 \times 10^{-24} m^2 A$
Electron charge	e	1.6022×10^{-19} C
Nuclear magneton	β_N	5.0504×10^{27} m^2 A

Appendix III

GREEK ALPHABETS

Alpha	A	α
Beta	B	β
Gamma	Γ	γ
Delta	Δ	δ
Epsilon	E	ε
Theta	θ	θ
Zeta	Z	ζ
Eta	H	η
Iota	I	ι
Kappa	K	κ
Lambda	Λ	λ
Mu	M	μ
Nu	N	ν
Xi		ζ
Pi	Π	π
Rho	P	ρ
Phi	Φ	ϕ
Psi	ψ	ψ
Omega	Ω	ω

Appendix IV

ENERGY CONVERSION TABLE

	erg mole^{-1}	*kcal mole*$^{-1}$	*eV*	*cm*$^{-1}$
1 erg molecule^{-1}	1	1.44×10^{13}	6.24×10^{11}	5.04×10^{19}
1 kcal mole^{-1}	6.95×10^{-14}	1	4.34×10^{-2}	350
1 eV	1.60×10^{-12}	23.1	1	8068
1 cm^{-1}	1.99×10^{-16}	2.86×10^{-3}	1.24×10^{-4}	1

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LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
10	0000	0043	0086	0128	0170						5 9 13	17 21 26	30 34 38
						0212	0253	0294	0334	0374	4 8 12	16 20 24	28 32 36
11	0414	0453	0492	0531	0569						4 8 12	16 20 23	27 31 35
						0607	0645	0682	0719	0755	4 7 11	15 18 22	26 29 33
12	0792	0828	0864	0899	0934						3 7 11	14 18 21	25 28 32
						0969	1004	1038	1072	1106	3 7 10	14 17 20	24 27 31
13	1139	1173	1206	1239	1271						3 6 10	13 16 19	23 26 29
						1303	1335	1367	1399	1430	3 7 10	13 16 19	22 25 29
14	1461	1492	1523	1553	1584						3 6 9	12 15 19	22 25 28
						1614	1644	1673	1703	1732	3 6 9	12 14 17	20 23 26
15	1761	1790	1818	1847	1875						3 6 9	11 14 17	20 23 26
						1903	1931	1959	1987	2014	3 6 8	11 14 17	19 22 25
16	2041	2068	2095	2122	2148						3 6 8	11 14 16	19 22 24
						2175	2201	2227	2253	2279	3 5 8	10 13 16	18 21 23
17	2304	2330	2355	2380	2405						3 5 8	10 13 15	18 20 23
						2430	2455	2480	2504	2529	3 5 8	10 12 15	17 20 22
18	2553	2577	2601	2625	2648						2 5 7	9 12 14	17 19 21
						2672	2695	2718	2742	2765	2 4 7	9 11 14	16 18 21
19	2788	2810	2833	2856	2878						2 4 7	9 11 13	16 18 20
						2900	2923	2945	2967	2989	2 4 6	8 11 13	15 17 19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2 4 6	8 11 13	15 17 19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2 4 6	8 10 12	14 16 18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2 4 6	8 10 12	14 15 17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2 4 6	7 9 11	13 15 17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2 4 5	7 9 11	12 14 16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2 3 5	7 9 10	12 14 15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2 3 5	7 8 10	11 13 15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2 3 5	6 8 9	11 13 14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2 3 5	6 8 9	11 12 14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1 3 4	6 7 9	10 12 13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1 3 4	6 7 9	10 11 13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1 3 4	6 7 8	10 11 12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1 3 4	5 7 8	9 11 12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1 3 4	5 6 8	9 10 12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1 3 4	5 6 8	9 10 11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1 2 4	5 6 7	9 10 11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1 2 4	5 6 7	8 10 11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1 2 3	5 6 7	8 9 10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1 2 3	5 6 7	8 9 10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1 2 3	4 5 7	8 9 10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1 2 3	4 5 6	8 9 10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1 2 3	4 5 6	7 8 9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1 2 3	4 5 6	7 8 9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1 2 3	4 5 6	7 8 9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1 2 3	4 5 6	7 8 9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1 2 3	4 5 6	7 8 9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1 2 3	4 5 6	7 7 8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1 2 3	4 5 5	6 7 8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1 2 3	4 4 5	6 7 8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1 2 3	4 4 5	6 7 8

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	123	456	789
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1 2 3	3 4 5	6 7 8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1 2 3	3 4 5	6 7 8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1 2 3	3 4 5	6 7 7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1 2 2	3 4 5	6 6 7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1 2 2	3 4 5	6 6 7
55	7404	7412	7419	7427	7435	7443	7461	7459	7466	7474	1 2 2	3 4 5	5 6 7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1 2 2	3 4 5	5 6 7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1 2 2	3 4 5	5 6 7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1 1 2	3 4 4	5 6 7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1 1 2	3 4 4	5 6 7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1 1 2	3 4 4	5 6 6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1 1 2	3 4 4	5 6 6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1 1 2	3 3 4	5 6 6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1 1 2	3 3 4	5 5 6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1 1 2	3 3 4	5 5 6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1 1 2	3 3 4	5 5 6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1 1 2	3 3 4	5 5 6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1 1 2	3 3 4	5 5 6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1 1 2	3 3 4	4 5 6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1 1 2	2 3 4	4 5 6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1 1 2	2 3 4	4 5 6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1 1 2	2 3 4	4 5 5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1 1 2	2 3 4	4 5 5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1 1 2	2 3 4	4 5 5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1 1 2	2 3 4	4 5 5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1 1 2	2 3 3	4 5 5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1 1 2	2 3 3	4 5 5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1 1 2	2 3 3	4 4 5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1 1 2	2 3 3	4 4 5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1 1 2	2 3 3	4 4 5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1 1 2	2 3 3	4 4 5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1 1 2	2 3 3	4 4 5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1 1 2	2 3 3	4 4 5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1 1 2	2 3 3	4 4 5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1 1 2	2 3 3	4 4 5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1 1 2	2 3 3	4 4 5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1 1 2	2 3 3	4 4 5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	1 1 2	2 3 3	4 4 5
88	9145	9450	9455	9460	9465	9469	9474	9479	9484	9489	0 1 1	2 2 3	3 4 4
89	9494	9499	9504	9509	9515	9318	9523	9528	9533	9538	0 1 1	2 2 3	3 4 4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0 1 1	2 2 3	3 4 4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0 1 1	2 2 3	3 4 4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0 1 1	2 2 3	3 4 4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0 1 1	2 2 3	3 4 4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0 1 1	2 2 3	3 4 4
95	9777	9782	9736	9791	9795	9800	9805	9809	9814	9818	0 1 1	2 2 3	3 4 4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0 1 1	2 2 3	3 4 4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0 1 1	2 2 3	3 4 4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0 1 1	2 2 3	3 4 4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0 1 1	2 2 3	3 3 4

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
·00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
·01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

ANTILOGARITHMS

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·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
·52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
·55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
·56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
·57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
·58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
·59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
·60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4893	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
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